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#### New Blue Emissive Conjugated Small Molecules with Low Lying

#### **HOMO Energy Levels for Optoelectronic Applications**

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#### Abstract

Versatile conjugated small molecules bearing cyanopyridone core (**CP1-5**), composed of various donor/ acceptor moieties at position -4 and -6 have been designed, developed and characterized. Their solvatochromic studies were conducted and analyzed using Lippert-Mataga, Kamlet-Taft and Catalan solvent scales and interesting results were obtained. The polarizability/ dipolarity of the solvent greatly influenced the spectra. The electrochemical studies were carried out using cyclic voltammetry to calculate the HOMO-LUMO energy levels. The study revealed that the synthesized conjugated small molecules possess low lying HOMO energy levels which can be exploited for application in various fields of optoelectronics.

Keywords: Cyanopyridone; Photophysical Properties; Solvatochromisim; Cyclic Voltammetry.

#### Introduction

Conjugated small molecules have been a subject of intensive research in the recent years owing to its vast application in biological imaging probes, sensors, lasers, light emitting devices [1-3] and light-energy harvesting [4, 5]. Thus, the development of novel conjugated small molecules (CSM) has attracted a great attention. Of the various types of CSM's, the molecules containing electron donors (D) and acceptors (A) connected by a  $\sigma$  bond or by a  $\pi$ -electron bridge (D-A-D or D- $\pi$ -A) are of substantial interest for optoelectronic devices [6, 7] such as light emitting diodes [8-10], solar cells [11-13] or electro generated chemiluminescence [14, 15]. In fact, synthetic [16] and theoretical [17, 18] investigations have clearly indicated that the introduction of aromatic and hetero aromatic systems bearing different electronic properties while designing a donor-acceptor (D-A) molecular frameworks may lead to the development of new CSM materials possessing unusual electrochromic, photochromic or luminescent behaviors. In this context, D-A systems show excellent photophysical properties because of their push-pull nature. Here, the molecular property of chromophores depends mainly on the strength of "pushpull" effect (i.e. the ability of the donor to provide electrons and the acceptor to withdraw electrons).

Pyridines are privileged structures because of their ubiquity in a wide span of natural products [19, 20]. Additionally, their chemical reactivity as a result of the ring aromaticity, presence of ring nitrogen atom,  $\pi$ -deficient nature of the ring, large permanent dipole moment, presence of electron deficient carbon atom which centers at the  $\alpha$  and  $\beta$  position invites attention for it to be probed as an acceptor [20]. Interestingly, cyanopyridines and cyanopyridones belong to the class of substituted pyridines which are known to display excellent thermal and photochemical stability [21, 22], high luminescence efficiency [21] and novel optoelectronic

properties [23]. In fact, the cyano group is known for its good electron withdrawing ability, small size and excellent stability under UV irradiation which will further increase the ability of the acceptor [1]. In view of their considerable photophysical potential, 3-cyanopyridines have been investigated for their viability as photoactive materials for use in a variety of applications [24-27]. As well, pyridine-2-ones are well known for their uniqueness of their tautomeric structure [10] [28] and fluorescence efficiency with high quantum yield [10, 21, 29].

The characterization of the compounds using simple photophysical studies may reveal fascinating facts about their luminescent properties. In this perspective, solvatochromic study of the compounds is necessary in order to understand the phenomenon of solute-solvent interactions and photophysical characteristics of a D-A molecule. These studies may be well examined by the utilization of solvent scales like Lippert-Mattaga [30-33], Kamlet-Taft and Catalán scales [34-37].

In the present work, we report five new cyanopyridone-based CSM's with tunable photophysical properties such as molar absorptivity, Stokes shift and quantum yield. These CSM scaffold possess easily-interchangeable electron-donating and electron-accepting groups in order to provide the obligatory architectures with tunable photophysical behavior. The photophysical properties of cyanopyridone derivatives were examined in a wide variety of solvents, including apolar, polar-protic and polar-aprotic solvents. Further, the effect of the solvent on the absorption and emission spectra are analyzed by a multi-component linear regression, wherein, several solvent parameters are simultaneously analyzed. Finally, the fluorescence quantum yield, the Stokes shift, optical band gap, electrochemical band gap as well as their HOMO-LUMO energy levels are analyzed to look for the suitability of these derivatives in optoelectronic devices.

#### **Experimental Section**

#### **Materials and Methods**

All the chemicals used in the present work were procured from commercial source. The reagents and solvent were used without further purification. The target compounds were purified and recrystallized from analytical grade solvents. UV-visible absorption and emission properties were measured using UV-1800 SHIMADZU UV-spectrophotometer and RF-5301 PC, SHIMADZU spectrophotometer equipped with a Xe-lamp as an excitation source, respectively. IR spectra were collected using Bruker ALPHA eco-ATR-IR on ZnSe Crystal. All the compounds were characterized by <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) on a Bruker spectrometer. The spectra were recorded at room temperature in deuterated chloroform (CDCl<sub>3</sub>) or deuterated dimethyl sulfoxide (DMSO- $d_6$ ). The chemical shifts are expressed in ppm values referenced to tetramethysilane (TMS). ESI-MS measurements were made on Waters (SYNAPT G2) with methanol as eluent.

Cyclic voltammetry (CV) data were determined in a N<sub>2</sub>-saturated three-electrode system, where, the working, counter and reference electrodes are glassy carbon, platinum and Ag/Ag<sup>+</sup>, respectively. The glassy carbon electrode was polished with 1.0 $\mu$ m alumina slurry and then sonicated for 10 min in distilled water. The CSM solution (in chloroform) was drop casted on to the glassy carbon disk and dried to get a uniform thin film of CSM, which was later dipped into acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. Further, the electrochemical measurements were made at a scan rate of 50 mV/s. The Ag/Ag<sup>+</sup> reference electrode was calibrated using a ferrocene/ ferrocenium (Fc/Fc<sup>+</sup>) redox couples as an external standard.



Scheme 1: Synthetic route for cyanopyridone (CP1-5) derivatives.

**Procedure for the preparation of cyanopyridone derivatives (CP1-5):** A mixture of aromatic/ heteroaromatic aldehyde **1a-d** (0.01 mol), acetyl aromatic/ heteroaromatic **2a-e** (0.01 mol), ethyl cyanoacetate (0.01 mol) and ammonium acetate (0.08 mol) in 1,4-dioxane (40 ml) was refluxed for 20 h (**Scheme 1**). The obtained precipitate was filtered, washed successively with 1,4dioxane, followed by ethyl acetate and finally recrystallized from ethanol-chloroform mixture to get the pure product (**CP1-5**).

2-Oxo-4,6-di-p-tolyl-1,2-dihydropyridine-3-carbonitrile (**CP1**): Pale yellow solid, yield 75 %, M.P. > 300°C. FTIR (cm<sup>-1</sup>): 2887, 2214, 1622, 1599, 1467, 807. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 12.68 (s, 1H, N<u>H</u> on heterocyclic), 7.76 (d, *J*=8 Hz, 2H, Ar-<u>H</u>), 7.61 (d, *J*=8 Hz, 2H, Ar-<u>H</u>), 7.35-7.29 (m, 4H, Ar-<u>H</u>), 6.73 (s, 1H, Ar-<u>H</u> (pyridine)), 2.35 (s, 6H, -C<u>H</u><sub>3</sub>). <sup>13</sup>C NMR (100 MHz, DMSO- $d_6$ )  $\delta$  (ppm): 162.5, 160.14, 160.12, 141.75, 140.81, 133.67, 129.92, 129.75, 128.61, 128.05, 117.10, 105.90, 21.36. MS (m/z) = 301 (M+H)<sup>+</sup>.

4,6-*Bis*(4-bromophenyl)-2-oxo-1,2-dihydropyridine-3-carbonitrile (**CP2**): Cream solid, yield 79 %, M.P. >300 °C. FTIR (cm<sup>-1</sup>): 3019, 2887, 2201, 1635, 1536, 807. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 7.87 (d, *J*=8 Hz, 2H, Ar-<u>H</u>), 7.72 (d, *J*=8 Hz, 2H, Ar-<u>H</u>), 7.64-7.61 (m, 4H, Ar-<u>H</u>), 6.83 (s, 1H, Ar-<u>H</u>(pyridine)). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  (ppm): 172.42, 165.38, 157.38, 153.36, 136.31, 134.25, 132.09, 130.78, 130.00, 124.64, 123.95, 117.82, 103.09, 96.75. MS (*m*/*z*) = 431 (M+H)<sup>+</sup>.

4,6-*Bis*(4-*nitrophenyl*)-2-*oxo*-1,2-*dihydropyridine*-3-*carbonitrile* (**CP3**): Yellow solid, yield 77 %, M.P. >300 °C. FTIR (cm<sup>-1</sup>): 3230, 2887, 2217, 1653, 1596, 1519, 851. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ (ppm): 8.32 (d, *J*=8 Hz, 2H, Ar-<u>H</u>), 8.28-8.22 (m, 4H, Ar-<u>H</u>), 7.88 (d, *J*= 8 Hz, 2H, Ar-<u>H</u>), 6.88 (s, 1H, Ar-<u>H</u> (pyridine)). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ (ppm): 156.32, 153.93,

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148.13, 148.03, 145.32, 145.24, 145.04, 130.09, 128.65, 124.03, 123.90, 104.60. MS (m/z) = 334 (M-NO)<sup>+</sup>.

6-(9*H*-fluoren-2-yl)-2-oxo-4-(thiophen-2-yl)-1,2-dihydropyridine-3-carbonitrile (**CP4**): Brownish yellow solid, yield 72 %, M.P. >300 °C. FTIR (cm<sup>-1</sup>): 2887, 2207, 1644, 1598, 1347, 830. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm): 12.75 (s, 1H, N<u>H</u> on heterocyclic), 8.04-8.03 (m, 2H, Ar-<u>H</u>), 7.94-7.85(m, 5H, Ar H) 7.31-7.29 (m, 3H, Ar-<u>H</u>), 7.24-7.22 (m, 1H, Ar-<u>H</u>), 3.30 (s, 2H, Ar-<u>H</u>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ (ppm): 161.5, 158.43, 153.48, 148.81, 130.18, 129.99, 129.71, 124.28, 124.15, 124.09, 116.49, 113.89, 103.70, 27.63. MS (*m*/*z*) = 349.08 (M-OH)<sup>+</sup>. 2-*Oxo-4*,6-*di*(*thiophen-2-yl*)-*1*,2-*dihydropyridine-3-carbonitrile* (**CP5**): Lemon Yellow solid, yield 82 %, M.P. >300 °C. FTIR (cm<sup>-1</sup>):3096,2887, 2209, 1630, 1593, 806.<sup>1</sup>H NMR (400 M Hz, DMSO-*d*<sub>6</sub>) δ (ppm): 12.75 (s, 1H, N<u>H</u> on heterocyclic), 8.03 (d, *J*= 4 Hz, 1H, Ar-<u>H</u>), 7.96 (d, *J*= 4 Hz, 2H, Ar-<u>H</u>), 7.94 (s, 1H, Ar-<u>H</u>), 7.86 (d, *J*= 4 Hz, 1H, Ar-<u>H</u>), 7.29 (t, *J*= 4 Hz, 1H, Ar-<u>H</u>), 7.23 (t, *J*= 4 Hz, 1H, Ar-<u>H</u>). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ (ppm): 152.42, 137.04, 131.85, 131.24, 131.22, 130.09, 130.07, 129.39, 129.06, 117.16. MS (*m*/*z*) = 285 (M+H)<sup>+</sup>.

#### **Results and Discussion**

#### **Synthesis**

Cyanopyridone derivatives (**CP1-5**) were synthesized in good yield (~72-82%) by a onepot method as shown in **Scheme 1**. The structures of synthesized compounds (**CP1-5**) were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectral analyses. Spectral data of all synthesized compounds were in full agreement with the proposed structures. IR spectrum of compound **CP1** showed absorption bands at 2887, 2214, 1622, 1599, and 1467 cm<sup>-1</sup> which were due to the C–H, C=N, C=O, C=N stretching's, and C–H bend, respectively. In general, the cyanopyridones can have the tendency to exhibit two tautomeric forms *i.e.* amidic and imidol

form. Further, the observed C=O peak stretching in IR spectra of compounds **CP1-5** clearly confirms that the compounds are in amidic form. Thus, the predominant solid state form is amidic form. In <sup>1</sup>H-NMR spectra, all protons were seen according to the expected chemical shift and integral values. The <sup>1</sup>H NMR spectrum of **CP1** showed a singlet at  $\delta$  11.39 corresponds to N-H proton of pyridone. The observed peaks in the range of  $\delta$  7.68-7.33 were attributed to aromatic protons. A singlet at  $\delta$  6.65 was due to pyridine 5H proton. Also, a singlet at  $\delta$  2.44 was due to methyl proton. Further, the mass spectrum of **CP1** showed molecular ion peak at m/z = 301 (M+H)<sup>+</sup>, which is in agreement with its molecular formula. Similarly, the spectral values for all the compounds are given in the experimental part.

#### **Photophysical Properties**

The UV-visible absorption spectra of **CP1-5** were recorded at the concentration of  $10^{-5}$  M in various solvents of increasing polarity to correlate the effect of solvent polarity on their absorption parameters. For this purpose, solvents of increasing polarity were selected (chloroform, ethylacetate, tetrahydrofuran (THF), methanol, dimethylformamide (DMF), acetonitrile, and dimethyl sulfoxide (DMSO)) based on their dielectric constants. The values of absorption maximum ( $\lambda_{max}^{abs}$ ) of **CP1-5** in these solvents are given in **Table 1**. UV-visible absorption spectra of **CP1** in various solvents are depicted in **Figure 1**. For all the compounds, the absorption bands were observed in the range of ~343-449 nm. The observed absorption bands can be attributed to  $\pi$ - $\pi$ \* transition.

From the **Table 1**, it is clear that the absorption maximum of the CSM is affected by solvent type. In case of **CP1**, **CP2** and **CP5**, only a slight red shift (~16-23 nm) with the increase in solvent polarity from chloroform to DMSO was seen. Whereas, a considerably increased red shift (~62 nm) is observed in case of **CP3** and a prominent red shift (~106 nm) is perceived in

case of **CP4** with the increase in solvent polarity. The spectral position of CSM's in various solvents further revealed interesting results. The absorption maximum  $(\lambda_{max}^{abs})$  is lowest in the case of chloroform, this is because, all other solvents used in this work are more polar than chloroform and can engage more strongly in a solute-solvent type of interaction. However, chloroform can interact with the CSM molecule in terms of dipole-dipole interactions, thereby, resulting in a net stabilization of the ground state of the CSM molecule, and hence one can see a hypsochromic shift in the spectrum. On the other hand, the absorption maximum  $(\lambda_{max}^{abs})$  value is shifted to lower energies *i.e.* bathochromic shift in highly polar solvents such as DMSO, because of stabilization of the excited state or the specific interaction between the solvent and hydrogen from NH group in the CSM molecule [38].



Figure 1: UV-visible absorption spectra of CP1 in various solvents.

However, anomalous behavior is observed in the absorption spectra of compounds **CP1**, **CP2** and **CP5** in methanol solvent where a hypsochromic shift is observed possibly due to the decrease of dipole movement upon excitation [39]. Cyanopyridone core has the ability to form intermolecular hydrogen bonding with the polar protic solvents. The hydrogen bonding in polar protic solvents can either increase in energy of ground state or decrease in the energy of exited state or both causing hypsochromic shift [40]. Also, the anomalous behavior is perceived in the absorption spectra of **CP1-5** in acetonitrile, wherein, hypsochromic shift is observed compared to that of DMF. This is due to the non-hydrogen donating property of acetonitrile where the solvation of CSM occurs through dipole-dipole interaction which generally causes the stabilization of the ground state [38]. Thus, this change in spectral position can be used as a probe for various types of interactions between the solute and the solvent. The molar absorptivity's were observed in the range of  $10 \times 10^2 - 56 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup> and is tabulated in **Table 1**.

CP1							
Solvent	$\lambda_{max}^{abs}(nm)$	$\lambda_{max}^{em}(nm)$	$E_g^{opt}$ (eV)	$\Phi_f$	Molar absorptivity $(L mol^{-1} cm^{-1})$		
Chloroform	370	441	3.34	0.02	$37 \times 10^{3}$		
Ethyl acetate	374	446	3.31	0.01	$29 \times 10^{3}$		
THF	374	446	3.30	0.02	$21 \times 10^{3}$		
Methanol	366	438	3.38	0.06	$56 \times 10^{3}$		
DMF	377	450	3.28	0.06	$18 \times 10^{3}$		
Acetonitrile	373	443	3.32	0.01	$55 \times 10^{3}$		
DMSO	383	450	3.23	0.10	$37 \times 10^{3}$		
CP2							
Chloroform	371	452	3.34	0.01	$19 \times 10^{3}$		
Ethyl acetate	377	452	3.28	0.02	$17 \times 10^{3}$		
THF	377	452	3.28	0.03	$12 \times 10^{3}$		
Methanol	368	448	3.36	0.11	$26 \times 10^{3}$		
DMF	388	464	3.19	0.25	$18 \times 10^{3}$		
Acetonitrile	373	453	3.32	0.02	$34 \times 10^{3}$		
DMSO	391	464	3.17	0.23	$27 \times 10^{3}$		

Table 1: Optical properties of CP1-5 in various solvents.

СРЗ						
Chloroform	386	475	3.21	0.05	$70 \times 10^2$	
Ethyl acetate	391	486	3.17	0.05	$80 \times 10^{2}$	
THF	395	492	3.13	0.06	$90 \times 10^{2}$	
Methanol	392	444	3.15	0.00	$12 \times 10^{3}$	
DMF	437	451	2.83	0.01	$60 \times 10^{2}$	
Acetonitrile	390	480	3.17	0.01	$10 \times 10^{3}$	
DMSO	448	446	2.76	0.02	$70 \times 10^2$	
		СР	4			
Chloroform	385	474	3.22	0.03	$15 \times 10^{3}$	
Ethyl acetate	394	484	3.14	0.03	$20 \times 10^{3}$	
THF	343	492	3.61	0.03	$24 \times 10^{3}$	
Methanol	394	438	3.14	0.01	$80 \times 10^{2}$	
DMF	440	457	2.83	0.01	$50 \times 10^{2}$	
Acetonitrile	389	486	3.19	0.02	$70 \times 10^{2}$	
DMSO	449	437	2.76	0.03	$40 \times 10^{2}$	
CP5						
Chloroform	397	469	3.12	0.40	$30 \times 10^{2}$	
Ethyl acetate	401	470	3.08	0.56	$20 \times 10^{2}$	
THF	404	472	3.06	0.76	$10 \times 10^{2}$	
Methanol	390	452	3.17	0.49	$40 \times 10^{2}$	
DMF	407	464	3.05	0.11	$20 \times 10^{2}$	
Acetonitrile	397	460	3.11	0.32	$40 \times 10^{2}$	
DMSO	414	468	3.00	0.61	$60 \times 10^2$	

The fluorescence spectra of **CP1-5** were also recorded at the concentration of  $10^{-5}$  M in various solvents of increasing solvent polarity (from chloroform to DMSO) and interesting results were obtained. The fluorescence emission spectra is not dependent on the variation in polarity of solvent. The fluorescence data is tabulated in **Table 1**. Fluorescence emission spectra of **CP1** in various solvents are shown in **Figure 2**. The compounds exhibit blue emission bands in the range of ~438-492 nm with Stokes shift of around ~14-149 nm. Remarkably, an anti-Stokes shift of 2 nm and 12 nm is observed from the compounds **CP3** and **CP4**, respectively in DMSO. It is important to note that, certain organic molecules where a  $\pi$ -conjugated bridge is end-capped by an electron-donor and electron-withdrawing group can show upconverted photon emission under specific conditions due to various processes [41]. In case of **CP3**, the acceptor

cyanopyridone unit was linked by two *para*-nitrophenyl units at its position -4 and -6 to form  $\pi$ conjugated donor-acceptor structure. Whereas, compound **CP4** composed of cyanopyridone
(acceptor), fluorenyl (donor) and thiophenyl (donor) units. In both the cases, observed antiStokes shift in DMSO solvent can be attributed to the photon upconversion process caused by
the nature of molecular architecture, the substituent effect, and modulation of the electronic and
geometric parameters [41].

In case of CP1 and CP2 only a small red shift (~ 12-16 nm) in the emission spectra was seen with the increase in solvent polarity from chloroform to DMSO. However, the largest emission maximum ( $\lambda_{max}^{em}$ ) of 450 and 464 nm is observed in case of CP1 and CP2 respectively in both DMF and DMSO. Whereas, in case of CP3, CP4 and CP5 the  $\lambda_{max}^{em}$  (444, 438 and 452 nm) is the least in polar protic solvent *i.e.* methanol. Among the polar aprotic solvents, a greater  $\lambda_{max}^{em}$  (492, 492 and 472 nm) is observed in case of **CP3**, **CP4** and **CP5** with THF. Further, the fluorescence quantum yield ( $\Phi_f$ ) of **CP1-5** in solution state was determined with reference to the standard procedure using quinine sulphate in 0.1 M sulfuric acid as a standard ( $\Phi_f = 0.54$ ) [42-44]. The CSM's displayed a wide range of quantum yields ( $\Phi_f = 0.01-0.76$ ), wherein, the highest quantum yield was exhibited by the compound CP5 in THF. Generally, the high quantum yield is attributed to the extent of planar conformation in the molecule. In case of CP5, the positions -4 and -6 of central cyanopyridone core are connected with the two small sized five membered thiophene ring. In addition, the steric hindrance caused by these five membered ring systems are less compared to that of the six membered or polycyclic aromatic hydrocarbon ring systems (*i.e.* substituted phenyl/ fluorenyl) connected to cyanopyridone at positions -4 and -6, respectively. Thus, compound **CP5** is possessing more planar conformation than that of the rest (**CP1-4**), which further result in the observed high quantum yield.



Figure 2: Fluorescence emission spectra of CP1 in various solvents.

In the present work, cyanopyridone chromophore bearing various electron donating (*i.e.* 4-methyl phenyl, 2-fluorenyl and 2-thiophenyl) and electron accepting groups (*i.e.* 4-bromo phenyl and 4-nitro phenyl) at positions -4 and -6 have been assembled to obtain D-A molecular architecture (**CP1-5**) with tunable photophysical behavior. From the results, only a slight change in photophysical properties were observed with change in the substituents. The bathochromic shift of **CP2** with respect to **CP1** or **CP3** with respect to **CP2** can be explained by the electron withdrawing characteristics of 4-bromo phenyl [45], or 4-nitro phenyl [46] group. In addition, bathochromic shift in **CP4** compared to **CP3** is due to the enhanced resonance stabilization caused by the fluorenyl ring [47] at position -4 and the electron donating capacity of thiophenyl ring at position -6 of cyanopyridone. A pronounced bathochromic shift is observed in case of **CP5** owing to its planarity and the electron donating capacity of the thiophenyl [48] substituents. As a whole, photophysical properties can be tuned and directed to the desired target by placing

electron withdrawing and electron donating substituents at suitable positions on the  $\pi$  - rich and  $\pi$ 

- deficient rings systems.

#### Lippert-Mataga plot (correlation between solvent polarity and Stokes shift)

The solvent induced spectral shifts caused by the general solvent effect is often interpreted using the Lippert – Mataga plot [30-33] of Stokes shift  $(\Delta v)$  versus orientation polarizability  $(\Delta f)$ .

eqn 1



Figure 3: Lippert-Mataga plot for CP1. The straight line represents the best linear fit to 7 data points.

The orientation polarizability (eqn 1) describes Stokes shift in terms of change in dipole moment of the fluorophore and the dependence of the energy of the dipole on the dielectric constant ( $\varepsilon$ ) and the refractive index of the solvent (n) [49]. The Lippert Mataga plot for **CP1** is shown in **Figure 3** as representative example and rest of the plots can be found in the supporting information. In all the cases, the plots were too scattered (r < 0.6) to allow to estimate the

difference between ground and excited states. Further, Kamlet Taft-Catalán scale were employed to account for the specific solvent interactions.

#### Kamlet Taft-Catalán scales

The specific solvent interactions are accounted most often using the Kamlet-Taft (eqn 2) [50] and Catalán (eqn 3) [50] solvent scales which can be expressed using the multiple linear equation.

$$y = y^{0} + a_{\alpha}\alpha + b_{\beta}\beta + c_{\pi^{*}}\pi^{*}$$
eqn2  
$$y = y^{0} + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SdP}SdP$$
eqn 3

According to the Kamlet-Taft solvent scale the parameters  $\alpha$ ,  $\beta$  and  $\pi$ \* are the measure of the specific interactions such as hydrogen bond accepting (acidity), hydrogen bond donating (basicity) and dipolarity/ polarizability, respectively, of a given solvent [34, 51]. The physiochemical parameters analyzed in the present work are the absorption maxima  $\overline{v}_{abs}$ , the emission maxima  $\overline{v}_{em}$  and the Stokes shift  $\Delta \overline{v} = \overline{v}_{abs} - \overline{v}_{em}$  (all in cm<sup>-1</sup>). The solvents used, Kamlet-Taft and Catalán parameters employed are tabulated in **Table 2**.

**Table 2:** Dielectric constant, refractive index, Kamlet- Taft ( $\alpha$ ,  $\beta$  and  $\pi^*$ ) and Catalán (SA, SB,

Solvent	3	η	α	β	π*	SA	SB	SP	SDP
Chloroform	04.8	1.45	0.20	0.10	0.58	0.047	0.071	0.783	0.614
Ethyl acetate	06.2	1.37	0.00	0.45	0.55	0.000	0.542	0.656	0.603
THF	07.9	1.41	0.00	0.55	0.58	0.000	0.591	0.714	0.634
Methanol	32.7	1.33	0.98	0.66	0.6	0.605	0.545	0.608	0.904
DMF	36.7	1.43	0.00	0.69	0.88	0.031	0.613	0.759	0.977
Acetonitrile	37.5	1.34	0.19	0.40	0.75	0.044	0.286	0.645	0.974
DMSO	46.7	1.47	0.00	0.76	1.00	0.072	0.647	0.830	1.000

SP and SdP) parameters for various organic solvents.

The multi-linear regression analysis of the physiochemical parameters employed as a function of the Kamlet – Taft solvent parameters were carried out on **CP1-5** and the estimated

coefficients  $y_0$ ,  $a_{\alpha}$ ,  $b_{\beta}$ ,  $c_{\pi^*}$  for **CP1** are summarized in **Table 3** (coefficient for **CP2-5** can be found in the supporting information). The multi-linear regression analysis of the  $\overline{v}_{abs}$  data of **CP1-5** in accordance to the Kamlet-Taft solvent scales provides a good linear fit measured by the value of  $r \sim 0.819$ -0.989. The negative value of both  $b_{\beta}$  and  $c_{\pi^*}$  (**Table 3**) indicates that there is positive solvatochromism which points to bathochromic shift with increase in solvent polarizability and solvent bond basicity. This suggests the stabilization of electronic state relative to the ground state [52, 53]. Also, a considerably better regression value  $r \sim 0.837$ -0.989 is observed with  $\overline{v}_{em}$  as a function of Kamlet-Taft parameters, the positive value of  $a_{\alpha}$  specifies a hypsochromic spectral shift with increasing hydrogen bond donating ability [53]. In case of  $\Delta \overline{v}$  as a function of Kamlet-Taft parameter the regression value r ranges from  $\sim 0.850 - 0.968$ .

In case of Catalán scale, the parameters SA, SB, SP and SdP represents the acidity, basicity, polarizability and dipolarity, respectively. From the **Table 3**, where the estimated coefficients  $a_{SA}$ ,  $b_{SB}$ ,  $c_{SP}$  and  $d_{SdP}$  are summarized, it can be observed that  $c_{SP}$ ,  $d_{SdP}$  have large negative values. This explains the large bathochromic shift with increase in solvent polarity and confirms the specific interaction of the excited state of molecule with the polar solvent [54]. Cyanopyridone derivatives owing to their tailor-made properties are of great interest for application in the field of optoelectronics [21, 29]. The result obtained for **CP1-5** indicates that it is possible to manipulate their fluorescence properties by tuning the substitution, the arrangement of functional groups and by the choice of appropriate solvents.

**Table 3:** Estimated coefficients  $(y^0, a_\alpha, b_\beta, c_{\pi^*}, a_{SA}, b_{SB}, c_{SP} \text{ and } d_{SdP})$ , their standard errors and correlation coefficients (r) for the multiple linear regression analysis of  $\Delta \overline{v}, \overline{v}_{abs}, \overline{v}_{em}$  of **CP1** as a function of the Kamlet-Taft (**eqn 2**) and Catalán (**eqn 3**) solvent scales. For Kamlet-Taft and Catalán, seven solvents were used in the analysis of  $\Delta \overline{v}, \overline{v}_{abs}, \overline{v}_{em}$ .

CP1							
Kamlet-Taft	$y^{\theta}$ (10 <sup>3</sup> )	$a_{\alpha}(10^3)$	$b_{\beta}(10^3)$	$c_{\pi^*}(10^3)$		r	
$\bar{\upsilon}_{abs}$	27.50±0.23	0.68±0.16	-0.42±0.30	$-0.95 \pm 0.40$		0.974	
$\bar{\upsilon}_{em}$	22.75±0.09	$0.51 \pm 0.06$	-0.46±0.11	-0.19±0.15		0.989	
$\Delta \bar{\upsilon}$	$4.74 \pm 0.26$	$0.17 \pm 0.18$	$0.04 \pm 0.33$	$-0.75 \pm 0.44$		0.853	
Catalán	$y^{\theta}(10^3)$	$a_{SA}(10^3)$	$b_{SB}(10^3)$	$c_{SP}(10^3)$	$d_{SdP}(10^3)$	r	
$\bar{\upsilon}_{abs}$	28.84±0.74	1.0±0.39	-0.7±0.34	-1.79±1.01	-0.68±0.41	0.967	
$\bar{\upsilon}_{em}$	23.43±0.23	$0.70\pm0.12$	$-0.62 \pm 0.10$	-0.73±0.31	-0.27±0.13	0.991	
$\Delta ar{\upsilon}$	5.41±0.79	0.30±0.42	-0.16±0.37	-1.07±1.10	-0.41±0.44	0.827	

#### **Cyclic Voltammetry**

Cyclic voltammetry (CV) is an effective tool to determine the molecular energy levels of CSM's, which is crucial for considering their abilities in terms of electron injection. CV measurements for **CP1-5** were carried out and the cyclic voltammetry curve of **CP2** in acetonitrile solution is shown in **Figure 4** (cyclic voltammetry curve of **CP1**, **CP3-5** are given in supporting information). For all the CSM's, reduction potential was observed, hence, LUMO of the CSM's were calculated using the formula  $E_{LUM0} = -[E_{onset}^{red} + 4.366 eV]$ , where  $E_{onset}^{red}$  are the observed onset reduction potentials verses standard calomel electrode (ionization potential for Fc/Fc<sup>+</sup> measured was 0.43 V vs. Ag/AgCl). The  $E_{onset}^{red}$  values obtained for **CP1-5** are tabulated in **Table 4**. On the other hand, oxidation potential observed only for **CP1**, **CP2** and **CP5** (1.77, 1.14 and 1.72 eV, respectively). Since, oxidation potential was not obtained for the **CP3** and **CP4**, to maintain uniformity the HOMO of the CSM was calculated using the optical band gap obtained from UV-visible spectra of **CP1-5** using the formula  $E_g = E_{LUM0} - E_{HOM0}$ . The energy levels and the electrochemical band gaps for the CSM's are tabulated in **Table 4**.

Sample	E <sup>red</sup> onset	E <sub>LUMO</sub> (eV)	E <sub>HOMO</sub> (eV)	E <sub>g</sub> (eV)
CP1	-0.55	-3.81	-7.13	3.31
CP2	-0.57	-3.78	-7.07	3.28
CP3	-0.50	-3.86	-6.93	3.06
CP4	-0.59	-3.77	-6.90	3.12
CP5	-0.55	-3.81	-6.91	3.10

Table 4: Electrochemical properties of CP1-5.



Figure 4: Cyclic voltammetry curve of CP2 in acetonitrile solution.

The sufficiently low HOMO energy levels of the CSM ensures its effective regeneration and suppress the recapture of the injected electrons by the CSM cation radical [55]. This property can be exploited in various application of CSM's. The energy levels of the synthesized CSM's are in accordance with that of the standard N719 dye and hence can be used as a co-sensitizer in preparation of dye sensitized solar cells.

#### Conclusion

In precise, we have designed and developed five new cyanopyridone based conjugated small molecules (CP1-5) featuring various donor and acceptor substituents at position -4 and -6 following appropriate synthetic routes. The reaction conditions were optimized and the purification techniques for all the new compounds were established. The solvatochromic behavior of the conjugated small molecules were investigated using seven solvents chosen based on their increasing dielectric constant and interesting results were procured. The absorption spectra revealed that all the compound showed a red shift with increasing solvent polarity while, the emission spectra was not significantly altered by increasing solvent polarity. These compounds were witnessed to be blue light emitting compounds. The observed Stokes shifts were correlated with solvent orientation polarizability using the Lippert-Mataga equation but, the plot were too scattered (r < 0.6) to allow the estimation of difference between ground state and excited state. Hence, to account for the specific solvent interactions Kamlet-Taft and Catalan solvent scales were employed and more linearly fit curve with better regression values ( $r \sim 0.8$ -0.9) were observed, wherein, the dipolarity/ polarizability greatly influence the solute-solvent interactions. Also, the result obtained for CP1-5 indicate that it is possible to manipulate their fluorescence properties by tuning the substitution, the arrangement of functional groups and by the choice of appropriate solvents. The band gap of these compounds were calculated using the data obtained from the photophysical studies. The frontier orbital examined with cyclic voltammetry revealed that the HOMO and LUMO of the conjugated molecule lie in the range of -6.90 to -7.13 eV and -3.77 to -3.86 eV, respectively. The sufficiently low HOMO energy level ensures the effective regeneration of the conjugated small molecules. All these results point out

that the synthesized cyanopyridone derivatives can be probed for application in the wide field of optoelectronics.

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#### Graphical Abstract



#### Highlights

- Versatile conjugated small molecules bearing cyanopyridone core were synthesized.
- Solvatochromic studies were conducted in seven organic solvents.
- Lippert-Mataga, Kamlet-Taft and Catalan solvent scales were used for determination of solute-solvent interactions.
- Synthesized conjugated small molecules possesses low lying HOMO energy levels.

A CERTINAN