Tuning of intermolecular interactions results in packing diversity in imidazolin-5-ones

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Abstract. Crystal structures of four *green fluorescent protein* (*GFP*) chromophore analogues with different packing interactions could be tuned by appropriate substitutions around the imidazolin-5-one ring are reported here. Compound **1** was crystallized from tetrahydrofuran at room temperature while compounds **2–4** have been crystallized from a mixture of methanol and dichloromethane in 3:1 ratio. Molecule **1**, **2** and **3** crystallized in monoclinic lattice while molecule **4** preferred to crystallize in a triclinic crystal system. The crystal packing of these molecules was stabilized by C-H... π stacking and C-H...O type of supramolecular interactions. The results reveal that packing diversity can be easily accomplished in these molecules by tuning the substituents around the imidazolin-5-one ring. Photophysical studies also reveal that all have good quantum yield and fluoresce typically in red region due to presence of electron donating groups around the imidazolin-5-one ring.

Keywords. Imidazolin-5-one; *gfp* chromophore; C-H... π stacking; hydrogen bonding; photophysical study.

1. Introduction

The imidazolin-5-one is the fluorophore present in the *green fluorescent protein* (*GFP*) from the *jellyfish* *Aequorea Victoria*¹ and is responsible for its application as a fluorescent probe.² In the *GFP* protein, *p*-hydroxybenzylideneimidazolinone (*p*-**HBDI**) is buried deep inside the protein β -barrel. In the native folded state of *GFP*, the chromophore is held planar and rigid by a network of intramolecular hydrogen bonds,³ thereby preventing radiationless decay, thus making *GFP* an efficiently fluorescent protein with a high quantum yield. Analysis of crystal structure as well as the π system reveals that the β -barrel of the protein plays a pivotal role in blocking this relaxation⁴ by preventing *cis-trans* isomerism of the exocyclic double bond.^{5,6}

In many of the *GFP* chromophore analogues studied previously C-H...O, C-H... π and π ... π interactions typically stabilize molecular arrangements into sheets,⁷ layers^{7b} or pyramidal structures⁸ in crystals. Donor-acceptor type of C=O...C interaction was also found to be a dominant short contact in one of the imidazolin-5-one derivative.⁹ The inter and intramolecular hydrogen bonding with different substituents at the chromophore influences not just the excited state dynamics to alter the fluorescence properties of the chromophore¹⁰ but also the crystal packing.^{6–9} *GFP* chromophore analogues

containing hydroxyl group as a substituent are weakly fluorescent in both solid¹¹ and in solution.¹² Imidazolin-5-ones with long alkyl chains are reported to be weakly fluorescent due to the lack of strong intermolecular short contacts.^{11a} In this study, we show how weak non-covalent intermolecular interactions such as C-H...O, C-H... π and π ... π stacking can be tailored in *GFP* chromophore to result in the formation of well-defined supramolecular structures. We also report the photophysical properties of these molecules in solution state.

2. Experimental

2.1 Materials

All solvents and chemicals were purchased from local company S.D. Fine Chemicals India Ltd. All chemicals were purified by literature recommended procedure.¹³ Sodium acetate was heated for 6–8 hours and cooled to room temperature in a desiccator and used while zinc chloride was dried by strong heating for 3–4 hours under reduced pressure and cooled to room temperature before the use for reactions. Acetic anhydride was used after distillation under high vacuum. Ethyl acetamide, triphenyl amine and NMR solvents were purchased from Sigma-Aldrich and used as such. Glycine was purchased from Merck chemical company and used as such.

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Silica gel of 60–120 and 100–200 mesh particle size and neutral alumina were purchased from MERCK, India and used for column chromatography. MERCK Kieselgel 60 F₂₅₄ plates were used for TLC analysis. ¹H NMR spectra were recorded by using JEOL 500 (500 MHz) and JEOL 400 (400 MHz) NMR spectrometer in CDCl₃ solvent, and proton decoupled ¹³C NMR spectra had taken in JEOL 500 (125 MHz) NMR spectrometer. Melting points of all (**1–4**) compounds were recorded in a JSGW melting point apparatus and were uncorrected. Mass spectra were taken in Water ESI-Q¹⁰ instrument. For absorption spectra measurement, Jasco V-550 UV-visible spectrophotometer was used and Fluorescence measurement was done in Fluorolog 3.21 spectrofluorimeter (Horiba Jobin-Yvon).

2.2 Synthesis of compounds (**1–4**)

All the molecules (figure 1) were synthesized by previously reported procedures.^{7,8,14–17} Molecule **1** was synthesized by solvent free Lewis acid catalyzed reaction.¹⁵ Molecule **2** has been synthesized in literature.¹⁶ Molecule **3** and **4** were synthesized followed by published procedure in literature.¹⁷

2.3 Spectroscopic characterization

2.3a (4Z)-4-(4-*N,N*-Dimethylaminobenzylidene)-1-decyl-2-phenyl-1,4-dihydro-5H-imidazolin-5-one (1**):** Red colour compound was obtained after column purification with isolated yield of 71%; compound

was recrystallized from THF and red needle shaped crystals were obtained, M.p. 70–72°C, *R*_f 0.5 (20% Ethyl acetate-petroleum ether). IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2924, 2854, 1689, 1630, 1588, 1524, 1490, 1371, 1191, 1155. ¹H NMR (CDCl₃, 500 MHz): δ 0.87 (t, *J* = 7.3 Hz, 3H, CH₃), 1.18–1.27 (m, 16, (CH₂)₈), 3.06 (s, 6H, N(CH₃)₂), 3.77 (t, *J* = 7.4 Hz, 2H, CH₂), 6.73 (d, *J* = 8.7 Hz, 2H, ArH), 7.22 (s, 1H, =CHAr), 7.51–7.52 (m, 3H, ArH), 7.77 (d, *J* = 7.8 Hz, 2H, ArH), 8.16 (d, *J* = 8.7 Hz, 2H, ArH). ¹³C NMR (CDCl₃, 125 MHz): δ 14.2, 22.7, 26.6, 29.1, 29.2, 29.3, 29.5, 29.6, 31.9, 40.1, 41.7, 111.8, 122.5, 128.4, 128.8, 130.5, 130.6, 130.7, 134.8, 135.1, 151.7, 159.4, 171.6. ESI-MS+ *m/z* Calcd. for C₂₈H₃₇N₃O: 432.3014 [M+H], found 432.3017.

2.3b (Z)-methyl 2-(4-(4-(dimethylamino)benzylidene)-2-methyl-5-oxo-4,5-dihydro-1H-imidazol-1-yl)acetate (2**):** Column purified orange colour compound was isolated in 75% yield; Further recrystallization of this compound from dichloromethane and methanol gave orange needle shaped crystals with a melting point of 220–225°C, *R*_f 0.5 (30 % Ethyl acetate-petroleum ether). IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 2907, 2822, 1748, 1686, 1639, 1595, 1558, 1413, 1379. ¹H NMR (CDCl₃, 500 MHz): δ 2.30 (s, 3H, CH₃), 3.04 (s, 3H, (CH₃)₂), 3.76 (s, 3H, CH₃), 4.38 (s, 2H, CH₂), 6.69 (d, *J* = 8.8 Hz, 2H, ArH), 7.11 (s, 1H, =CHAr), 8.05 (d, *J* = 8.9 Hz, 2H, ArH). ¹³C NMR (CDCl₃, 125 MHz): δ 15.5, 40.1, 41.4, 52.8, 111.8, 122.1, 129.9, 134.0, 134.4, 151.7, 157.7, 168.4, 170.1. ESI-MS+ *m/z* Calcd. for C₁₆H₁₉N₃O₃: 302.1505 [M+H], found 302.1458.

Figure 1. GFP chromophore analogues discussed here. Note that the analogues are different only in the substitution of the groups around the imidazolin-5-one ring. While compounds **1** and **2** are differing in the substitution at N(1) and C(2). **3** is a dimer of **2** while **4** has NPh₂ and a N-Ph group.

2.3c (4*Z*,4'*Z*)-1,1'-(ethane-1,2-diyl)bis(4-(4-(dimethylamino)benzylidene)-2-methyl-1*H*-imidazol-5(4*H*)-one) (**3**): Column purified yield of product was 70%; Red rod shaped crystals were obtained from dichloromethane-methanol mixture, M.p. 215–220°C, *R*_f 0.5 (40% Ethyl acetate-petroleum ether). IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3367, 2919, 2805, 1687, 1638, 1593, 1523, 1435, 1362, 1323. ¹H NMR (CDCl₃, 500 MHz): δ 2.20 (s, 6H, 2CH₃), 3.05 (s, 12H, 2(CH₃)₂), 3.86 (s, 4H, 2CH₂), 6.68 (d, *J* = 9.15, 4H, 2ArH), 7.08 (s, 2H, 2CHAr), 8.03 (d, *J* = 8.6, 4H, 2ArH). ¹³C NMR (CDCl₃, 125 MHz): δ 15.2, 39.3, 40.1, 111.8, 122.0, 129.8, 133.9, 134.3, 134.5, 151.8, 158.0, 170.9. ESI-MS+ *m/z* Calcd. for C₂₈H₃₂N₆O₂: 485.2665 [M+H], found 485.2668.

2.3d (Z)-4-(4-(diphenylamino)benzylidene)-2-methyl-1-phenyl-1*H*-imidazol-5(4*H*)-one (**4**): Column purified isolated yield was 70%; Recrystallization from dichloromethane-methanol mixture yielded orange rod shaped crystals, M.p. 202–205°C, *R*_f 0.5 (30% Ethyl acetate-petroleum ether). IR (KBr) $\nu_{\text{max}}/\text{cm}^{-1}$: 3430, 2925, 1718, 1640, 1585, 1488, 1387, 1360. ¹H NMR (CDCl₃, 400 MHz): δ 2.22 (s, 3H, CH₃), 7.03 (d, *J* = 8.7 Hz, 2H, ArH), 7.09 (t, 2H, ArH), 7.13–7.16 (m, 5H, ArH), 7.22–7.30 (m, 5H, ArH & 1H, CHAr),

7.39–7.43 (m, 1H, ArH), 7.47–7.51 (m, 2H, ArH), 8.02 (d, *J* = 8.7 Hz, 2H, ArH). ¹³C NMR (CDCl₃, 100 MHz): δ 16.5, 121.2, 124.3, 125.7, 127.2, 127.4, 128.2, 128.7, 129.5, 129.7, 133.6, 133.8, 136.1, 146.7, 149.8, 159.9, 170.0. ESI-MS+ *m/z* Calcd. for C₂₉H₂₃N₃O₁: 430.1919 [M+H], found 430.1912.

2.4 X-ray crystallography

The instrument used for data collection and the method adopted for structure solution and data refinement are same as those reported by our group earlier.⁸ Data has been deposited in the Cambridge crystal data centre and has the CCDC numbers 994598 (compound **1**), 994599 (compound **2**), 994600 (compound **4**) and 994601 (compound **3**).

3. Result and Discussion

3.1 Crystallographic studies

The X-ray crystal structure and refinement data of imidazolin-5-ones (**1–4**) are shown in table 1. In general, the *p*-hydroxybenzylidene imidazolin-5-one (*p*-HBDI) which is the nearest analogue of *GFP* chromophore, crystallized in monoclinic system. The

Table 1. Crystallographic data for molecules **1–4**.

Molecule	1	2	3	4
Formula	C ₂₈ H ₃₇ N ₃ O	C ₁₆ H ₁₉ N ₃ O ₃	C ₂₈ H ₃₂ N ₆ O ₂	C ₂₉ H ₂₃ N ₃ O ₁
Formula weight	431.61	301.34	484.60	429.50
Temperature/K	298	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>a</i> /Å	14.410(6)	15.800(5)	19.356(5)	9.6834(11)
<i>b</i> /Å	8.751(4)	10.421(5)	5.813(5)	10.6430(13)
<i>c</i> /Å	19.591(8)	9.563(5)	23.144(5)	12.6213(16)
$\alpha/^\circ$	90	90	90	90.283(3)
$\beta/^\circ$	96.146(8)	106.380(5)	109.012(5)	109.029(3)
$\gamma/^\circ$	90	90	90	113.272(3)
<i>V</i> /Å ³	2456.3(18)	1510.7(12)	2462(2)	1116.2(2)
<i>Z</i>	4	4	4	2
<i>D</i> _c /g cm ⁻³	1.167	1.325	1.307	1.278
μ /mm ⁻¹	0.071	0.093	0.085	0.079
<i>F</i> (000)	936	640	1032	452
Crystal size / mm	0.29 × 0.22 × 0.13	0.16 × 0.14 × 0.12	0.14 × 0.12 × 0.11	0.18 × 0.15 × 0.12
θ range/ $^\circ$	2.4–28.0	2.37–26.0	1.86–25.5	2.44–28.07
Reflections collected	15399	8362	6322	8314
Independent reflections	5854	2970	2277	4364
Data/restraints/parameters	5854/0/289	2970/0/235	2277/0/166	4364/0/299
Goodness-of-fit on <i>F</i> ²	0.948	1.067	1.102	0.873
Final <i>R</i> indices	<i>R</i> 1 = 0.0601	<i>R</i> 1 = 0.0565	<i>R</i> 1 = 0.0457	<i>R</i> 1 = 0.0564
[<i>I</i> > 2Sigma (<i>I</i>)]	<i>wR</i> 2 = 0.1567	<i>wR</i> 2 = 0.1753	<i>wR</i> 2 = 0.1472	<i>wR</i> 2 = 0.1636

Table 2. Interatomic distance(Å) and bond angle(°) observed in the structures **1-4**.

Molecule	D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	<D-H...A (°)	Symmetry codes
1	C(12)-H(12)...O(1)	0.93	2.57 (26)	3.408(26)	149(12)	1-x, -0.5+y, 0.5-z
	C(14)-H(14)...O(1)	0.93	2.58 (14)	3.284(24)	133(12)	x, 1.5-y, -0.5+z
2	C(15)-H(15B)...O(2)	0.97	2.43 (18)	3.197(4)	136	x, 0.5-y, 0.5+z
	C(21)-H(21B)...O(2)	1.01(4)	2.51(3)	3.390(4)	147(3)	x, 0.5-y, 0.5+z
3	C(2)-H(2A)...O(1)	0.96	2.40	3.268(4)	150	-0.5+x, 0.5+y, z
	C(14)-H(14A)...O(1)	0.97	2.57	3.526(4)	167	1-x, -y, -z
4	C(18)-H(18)...O(1)	0.93	2.53	3.221(3)	131	-1+x, -1+y, -1+z
	C(19)-H(19)...N(2)	0.93	2.55	3.387(4)	149	1-x, 1-y, -z

—*NMe*₂ substituted chromophore analogues **1**, **2** and **3** have been crystallized in monoclinic crystal system while —*NPh*₂ substituted compound **4** has crystallized in triclinic crystal system. The significant

intermolecular interactions observed in the crystal structures of molecules **1-4** are listed in table 2.

The ortep view of compound **1** is shown in figure 2a. In molecule **1**, the single bond between C(1)

Figure 2. (a) Ortep view of imidazolin-5-one (**1**) and the thermal ellipsoids are shown at 50% probability level. (b) Hydrogen bond between C(12)-H(12)...O(1) & C(14)-H(14)...O(1) extended the packing of the molecules. Colour code: dotted green line indicates C-H...O hydrogen bond. Other hydrogen atoms are free from short contact and these are omitted for clarity of the picture.

and C(11) carbon atom ensure a perpendicular orientation of the benzene ring from the molecular plane.

Consequently, this molecule is no longer superimposable on its own mirror image and takes a chiral

Figure 3. (a) Ortep view of molecule 2 with atom numbering. The thermal ellipsoids are shown at 50% probability level. (b) One dimensional layer structure formed through C(21)-H(21B) ... O(2) & C(15)-H(15B) ... O(2) hydrogen bonding. (c) Two dimensional arrangement through weak hydrogen bonding between H(21B) ... O(1) and C-H ... π interaction between benzene ring & H(20C) and imidazoline ring & H(19A). Dotted orange line indicates C-H ... O hydrogen bond and Green dotted line indicates C-H ... π interactions. Other hydrogen atoms are free from short contact and these are omitted for clarity of the picture.

conformation. Presence of equal amounts of opposite conformers of compound **1** makes the crystal space group achiral (table 1). The *N*-substituted decyl chain and *N,N*-dimethylaminobenzylidene groups resemble the wings of a flying butterfly. Previously, it has been reported by our group⁸ that the *N*(1)-methyl derivative shows a strong donor-acceptor type of $\pi \dots \pi$ stacking interaction whereas in molecule **1**, there is no $\pi \dots \pi$ stacking observed and this is because of the presence of the non-polar decyl chain. This is packed over the polar *N,N*-dimethylaminobenzylidene units (figure 2b).

The average distance of the decyl chain from the polar conjugated part is 3.86 Å. The C(12)-H(12) $\cdots$ O(1) ($d(\text{H} \cdots \text{O}) = 2.57$ Å) and C(14)-H(14) $\cdots$ O(1) ($d(\text{H} \cdots \text{O}) = 2.58$ Å) non-classical hydrogen bond interactions linearly extend the array in the crystal. Based on the analyses of the hydrogen bonds by Desiraju and Steiner,^{6a} the average stabilization energy of each of the C-H $\cdots$ O hydrogen bonds in molecule **1** can be supposed to be around -1.5 kcal/mol. As a result of the crystallization of the decyl chain over the conjugated system, the colour of the crystal is significantly enhanced to red.

Figure 4. (a) Ortep view of imidazolin-5-one (**3**) with atom numbering. The thermal ellipsoids are shown at 50% probability level. (b) One dimensional layer structure form by hydrogen bonding between C(14)-H(14A) $\dots$ O(1). (c) Dotted green line shows C(8)-H(8) $\dots \pi$ and C(13)-H(13) $\dots \pi$ bond and dotted orange line represent hydrogen bond between C(2)-H(2A) $\dots$ O(1). Other hydrogen atoms are omitted for clarity of the picture.

Molecule **2** formed orange coloured needles. The crystal structure of this molecule shows an extended two dimensional polymeric structure, wherein molecules pack in a head to head fashion, held together by weak hydrogen bonding and C-H... π interactions. The imidazolinone and substituted benzene rings help in the formation of a T-shape herringbone structure thereby facilitating C-H... π interactions (figure 3c). Methyl hydrogen of glycine methyl ester C(19)-H(19C) was bonded with the centroid of the imidazoline ring with a distance 2.71 Å and bond angle of 133.7°, while C(20)-H(20C) hydrogen formed a CH... π bond with *para* substituted benzene ring with the distance of 2.77 Å and bond angle of 142.8°. The weak intermolecular hydrogen bonding between O1 and H(21B)-C(21) (distance and angle being 2.62 Å and 129.6° respectively), was also observed. This formed two hydrogen bonds with molecules above and below to form a two dimensional supramolecular architecture. Apart from this hydrogen bonding interaction, two other additional hydrogen bonds O(2)...H(21B)-C(21) and O(2)...H(15B)-C(15) were also found with the bond length of 2.50 Å and 2.43 Å respectively. These two hydrogen bonds help the lattice to grow along the

Table 3. Photophysical data of compounds **1-4** in methanol at room temperature.

Compound	$\lambda_{\text{abs}}(\text{nm})$	$\epsilon(\text{M}^{-1}\text{cm}^{-1})$	$\lambda_{\text{emis}}(\text{nm})$	Q.Y.
1	459	31,100	541	2×10^{-3}
2	436	37,120	506	3.2×10^{-3}
3	436	36,300	509, 606	4.2×10^{-3}
4	438	28,213	606	1.1×10^{-2}

c-axis. Clark *et al.* have been studied the luminescent property of this molecule (**2**) in acetonitrile solvent¹⁶ and reported a quantum yield 3.4×10^{-4} .

Molecule **3** is akin to a dimer of *GFP*. Ortep diagram of the dimer shows the antiperiplanar orientation of both the units with respect to each other. This is probably because of sterics. The crystal structure of this molecule exhibits an extended two dimensional ladder shaped polymeric structure held by C-H... π and C-H...O type supramolecular interactions. Unlike molecule **2** where the imidazolin-5-one ring forms C-H...O interactions, the C-H... π interactions are observed both above and below the plane of the *para*-substituted benzene ring in molecule **3** (figure 4).

Figure 5. (a) Ortep view of imidazolin-5-one (molecule **4**) with atom numbering. The thermal ellipsoids are shown at 50% probability level. (b) Dotted green line shows hydrogen bonding between C(18)-H(18)...O(1) and C(19)-H(19)...N(2) atoms extend the molecules in one dimension. Other hydrogen atoms are free from short contact and these are omitted for clarity of the picture.

Aromatic C(8)-H(8)⋯ π bond is slightly longer 2.92 Å in compound **3** compared to methyl C(13)-H(13C)⋯ π bond which is 2.66 Å. Oxygen of imidazolinone ring O(1) also engages in the hydrogen bonding with hydrogen atom H(2A) of methyl group with a bond length of 2.40 Å and a bond angle of 150°. The presence of other hydrogen bonding C(14)-H(14A)⋯O(1) with bond length 2.57 Å and angle 166.7°, arranges

this molecule in a sheet like structure in one dimension in the crystal.

In molecules **1-3**, $-NMe_2$ group acts as an electron donor and these molecules are almost planar except molecule **1**, while in molecule **4**, $-NPh_2$ group distorts the molecule from planarity and makes the molecular conformation chiral. Here, however, the presence of equal amounts of chirally opposite conformers is

Figure 6. (a) UV-absorption spectra. (b) Fluorescence spectra of compound **1-4**.

responsible for resulting in an achiral unit cell in the crystal with P-1space group. This molecule gives a one dimensional arrangement through hydrogen bonding. Both nitrogen and oxygen of the imidazolinone ring are involved in hydrogen bonding. Surprisingly, $\pi\cdots\pi$ or C-H $\cdots\pi$ type of interactions were not observed within the structure despite the molecule having five aromatic rings (including the imidazole ring) being present. The imidazole ring is involved in $\pi\cdots\pi$ stacking in several structures reported from our group.^{7b} The carbonyl oxygen (O1) forms a weak hydrogen bond (C(18)-H(18) $\cdots$ O(1)) with an aromatic hydrogen atom (distance 2.53 Å and angle 130.9°), while the nitrogen (N2) atom forms C(19)-H(19) $\cdots$ N(2) intermolecular hydrogen bond with the corresponding distance of 2.55 Å and an angle of 149.3°.

3.2 Photophysical studies

Photophysical properties of these compounds (**1-4**) were measured in methanol solvent at room temperature. The compounds (**2-4**) have similar absorption maxima (λ_{max}) compared to compound **1**, which absorbs at slightly higher wavelength ($\lambda_{\text{max}} = 459$ nm) (figure 6a). The higher value of molar extinction coefficient of molecules **2-4** in comparison to molecule **1** at the lower wavelength and reinforces a strong electronic delocalization in these molecules (table 3).¹⁸

All the compounds are well fluorescent and recorded in 10 μM concentration in methanol solvent. These molecules support the concept of involvement of methyl rotors in the deactivation mechanism reported by Gepshtein *et al.*¹⁹ They have proposed that barrier less rotation of methyl group at *N*- and *C*- of the imidazolinone ring in *GFP* chromophore is an additional factor for the fluorescence quenching.²⁰ Here, in all the compounds, nitrogen atom of the imidazolinone is substituted by bulky group instead of methyl group. The fluorescence spectra of *N,N*-diphenylamine derivative (molecule **4**) has highest quantum yield of 0.011 at emission maximum 606 nm in compared to *N,N*-dimethyl derivatives (molecule **1**, **2** and **3**), this is because the extended conjugation (*N,N*-diphenylamine) at nitrogen of *para* substituted benzene ring increases the electron density at the σ bond between *para* substituted benzene ring and *N,N*-diphenylamine moiety, which provides rigidity to the molecule **4** (figure 6).^{5b}

4. Conclusion

The results thus reveal that changing the substitution from $-\text{NMe}_2$ to $-\text{NPh}_2$ changes the interactions

of these molecules in crystals. Similarly, changing a *N*-phenyl ring to an aliphatic chain or methyl acetate also modulates the packing due to the presence of differently capable substituents. Compound **1** and **4** forms a supramolecular one dimensional architecture stabilized by non-classical hydrogen bonding. On the other hand compound **2** and **3** are planar and assembling into two dimensional architectures via both C-H $\cdots\pi$ and hydrogen bonding interactions. Photoluminescence studies of these molecules have also been done in solution state and observed that molecule **4** is having highest quantum yield 0.011 with emission maxima 606 nm due to extended conjugation.

Supplementary Information

Supplementary material contains all ^1H and ^{13}C spectra, cif and cif check files. The final CIF files were deposited at Cambridge Crystallographic Data Centre and the CCDC numbers are reported in the manuscript. Figures S1–S4 can be seen at www.ias.ac.in/chemsci.

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