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General solvent-free ionic liquid catalyzed C–N/C–C coupled cyclization to diverse dihydropyrimidinones and new organic materials: Langmuir–Blodgett film study†

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An ionic liquid catalyzed dual C–N/C–C coupled cyclization of a three component assembly is demonstrated to access 3,4-dihydropyrimidin-2(1*H*)-one (DHPM) analogues under solvent-free green conditions. Innovative new organic materials are introduced with pure and mixed DHPM using LB high surface pressure, AFM and photophysical studies.

Organic compounds possessing aggregation properties have attracted the attention of research, fabrication, production and business communities as futuristic materials for next generation electronic devices. Organic molecules are quite innovative components for designing materials for high-tech devices of ultimate sensitivity because of their structural diversity leading to much improved semiconducting, conducting, non-conducting, photoluminescence, storage and display performances relative to silicon, copper and other traditional ingredients.[1–5] They are also lighter, more flexible, non-magnetic, biodegradable and inexpensive with respect to their inorganic counterparts. Benzimidazoles, imidazoles, porphyrins, and other N-heterocycles are utilized as the main building blocks for organic electronics.[2] Introducing an ubiquitous framework dihydropyrimidinone (DHPM)[6]-bearing several nanoscale gluing interactions[2b] (**E**, Fig. 1) into the active research area is desirable to achieve new organic materials for fabricating innovative devices. With the current global awareness of developing environment friendly green industrial technologies,[7] it is urgent to divert our attention from multistep organic syntheses into the nonhazardous multi-component strategy[8c] towards green synthesis[7–10] of functional molecules through development of solvent-free[8a] non-metallic processes such as using ionic liquid (IL)[9,10] as a green solvent *cum* catalyst, which found scant application.[10] Recent medicinal research found DHPMs as active pharmaceutical agents for epilepsy (**A**, Fig. 1), antihypertensive calcium ion channel blocker (**B**), prostatic hyperplasia (**C**), cancer (**D**), fungal, viral, bacterial, inflammatory and cardiovascular diseases.[6,11,12] The syntheses of valuable DHPMs were achieved by Biginelli[11] and Biginelli-type coupling of aldehyde, urea/thiourea and β-dicarbonyl compounds using mineral acids, Lewis acid catalysts, nanoparticles, IL, solvent-free and/or catalyst-free conditions.[12]

Hitherto, all these methodologies come up with drawbacks using volatile organic solvents, excess quantity of IL, exhaustive usage of energy sources (*e.g.* high temperature), prolong reaction time, tedious catalyst preparation and isolation, formation of inevitable side products, and/or insufficient yield. With these difficulties in mind we developed a general solvent-free C–N/C–C coupled fundamental annulation process[13] to DHPM analogues (Scheme 1) using protic ionic liquid as a catalyst. The preliminary results on LB study, aggregation property and surface morphology of the first ever DHPM-based materials are reported.

We decided to begin with an easily affordable protic IL catalyst such as imidazolium trifluoroacetate derivatives for developing a solvent-free green cyclization strategy of a three component assembly comprising benzaldehyde (R^1 = Ph, **1a**, Scheme 1), urea (X = O, **2a**) and ethyl acetoacetate (R^2 = OEt, **3a**) to afford the desired DHPM (**4a**) and the successful annulation approach will be generalized and diversified through direct synthesis of varied functionalized and chiral DHPMs, their thio analogues and also the designed DHPMs of potential material properties (**E**, Fig. 1). Gratifyingly after a limited number of attempts we found rapid (30 min, entry 1, Table 1) conversion (100%) of the ingredients into the desired product **4a** (entry 1) at moderate temperature (70 °C) using 10 mol% of PIL, 2-methyl-1-butyl imidazolium trifluoroacetate (**I**, Scheme 1). Interestingly

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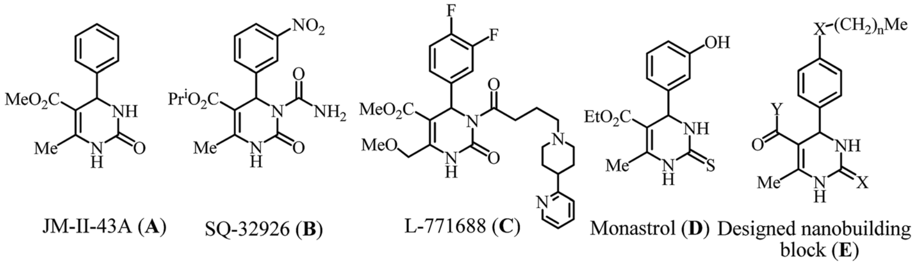
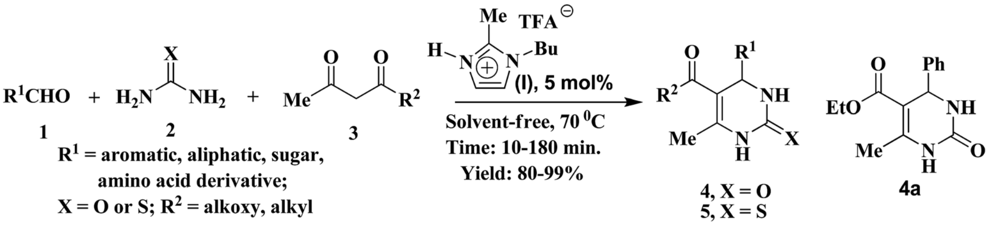


Fig. 1 Medicinally significant and potential material DHPMs.



Scheme 1 A rapid C–N/C–C coupled annulation strategy to DHPMs.

progress of the reaction was ascertained simply by watching slow deposition of the solid product, which started within a couple of minutes. Comparable yield (89%) was obtained on reduction of catalyst loading from 10 to 5 mol% (entry 2). However the yield was reduced (entries 3 and 4) on further decrease of IL concentration (4–1 mol%), and no product was detected in absence of IL, heat or using Bu_4NBr and BMImCl (entries 5–8). A plot for PIL (I) concentration *vs.* conversion of the starting material is included in the ESI.† However other ionic liquid such as $BMImBF_4$ and $BMImPF_6$ (ref. 9b) producedthe desired product with moderate yield (52–56%; entries 9 and 10) at high temperature. Thus, the results showed in Table 1 indicated that protic ionic liquid (**I**) offers best results than the other ionic liquid. We speculate that this is due to capability of protic ionic liquid **I** to activate carbonyl group[11c,d] of aldehydes which speeds up the iminium ion (**X**) formation with urea or thiourea and subsequent nucleophilic addition to the protic ionic liquid activated enolized-β-keto ester followed by cyclization (**Z**) and elimination of water results the expected DHPM (Scheme 2). Lacking of proton in other ionic liquids, carbonyls of aldehydes/β-dicarbonyls either not or less efficiently activated thus they required high temperature and long reaction time.

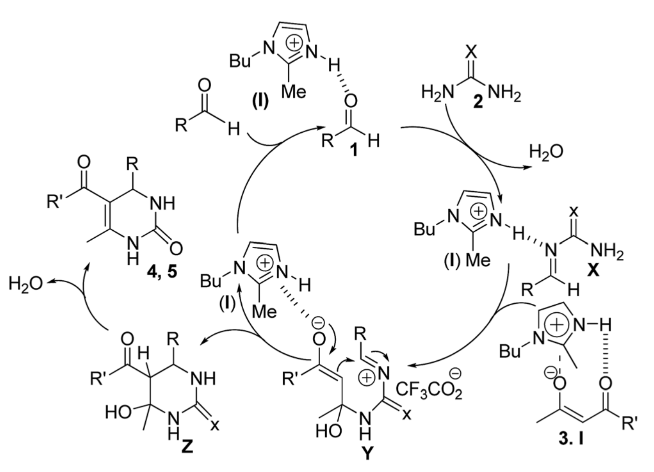
The scope and versatility of the green strategy was successfully examined with a wide range of precursors towards rapid (10–90 min) access to functionalized DHPMs (**4b–s**, Fig. 2) with excellent yield (84–99%). A broad range of DHPMs possessing electron donating and electron withdrawing functionality substituted phenyl (**4b–l**), naphthyl (**4m**), conjugated π-bond (**4n**), and aliphatic substituents (**4o–q**) were synthesized. Acetyl acetone, flexible chiral aldehyde and thiourea were also smoothly underwent for the dual C–N/C–C coupling process to furnish corresponding DHPMs possessing acetyl group (**4r** and **4s**), chiral amine-based **4t** with about 3 : 1 diastereomer ratio and thione analogues (**5a–e**). To our delight the outstanding stereo-selection ability of the non-metallic PIL catalyst was observed to furnish optically pure single diastereomer **4u** from structurally rigid chiral sugar aldehyde. Absolute stereochemistry (**4u**) was determined by NMR spectroscopic analysis (ESI†). In general, the reactions are very clean, generate no by product except water, furnish highly pure products after simple washing with water and require no chromatographic separation. However, poor solubility of urea hampered the precipitation process of the product leading to formation of impure material in few reactions. On dissolving urea in a little amount of water (0.5 mL) solved the problem without changing the reaction rate and yield. Alternatively crystallization in ethanol can be used to afford pure DHPM. The designed DHPM-bearing ester, long-chain alkoxy, donor HN–CO–NH, π-bond and aromatic moiety (**4v**) and its thio analogue (**5f**) were achieved under similar conditions.

We investigated the aggregation behaviour of **4v** by using LB technique[3] because it can efficiently be used for making films of controllable thickness, uniform surface and a high degree of orientational order of pure **4v** and mixed DHPM–arachidic acid (AA). The mixed monolayers with AA[3e] was attempted for examining the valuable monolayer stability, second harmonic generation effects, pyroelectric, photochromic and intermolecular interactive properties. In our experiments, we observed that on spreading out of a dilute solution of pure **4v** in chloroform (2×10^{-3} M) onto a pure water surface and compressing slowly resulted an initial rise of isotherm from zero to about 25 mN m^{-1} (Fig. 3A). A kink was observed and enhanced sharply to 55 mN m^{-1}. The surface pressure *versus* area per molecule (π–A) isotherms of pure AA and **4v**–AA mixed monolayers were executed (Fig. 3B) at the air–water interface. The abscissas of these figures represented the area of Langmuir film divided by the total

Table 1 Optimization for synthesis of DHPM (**4a**)[a]

Entry	Catalyst (mol%)	Temperature (°C)	Time (min)	Conversion (%)	Yield[b] (%)
1	**I** (10)	70	30	100	90
2	**I** (5)	70	30	100	89
3	**I** (1)	70	300	60	40
4	**I** (4)	70	300	90	81
5	None	70	300	—	0
6	**I** (5)	30	300	—	0
7	Bu_4NBr[c]	100	30	—	0
8	BMImCl[c]	100	30	—	0
9	$BMImBF_4$[c]	100[d]	60	90	56
10	$BMImPF_6$[c]	100[d]	60	80	52

[a] 10 mmol scale. [b] Isolated yield. [c] 10 mol%. [d] No reaction at 70 °C.



Scheme 2 PIL (I) catalytic cycle for synthesis of DHPMs.

number of the molecules, $N = N_{\text{EMT}} + N_{\text{AA}}$, where $N_{4\text{v}}$ and N_{AA} are the numbers of **4v** and AA molecules respectively. The pure AA isotherm was consistent with the behaviour expected from the previous measurements of this system. The isotherm of pure AA was resulted the limiting area of 0.20 nm^2 indicating vertical standing of the long-chain fatty acids on water. The isotherm of pure **4v** is very different to that of AA and no kink was observed. On mixing **4v** with AA, the DHPM inserted into the monolayer, which was confirmed by changing in the lift off point and the existence of kink point in the mixed isotherm at about 25 mN m^{-1}. The π–A isotherms of the **4v**–AA mixed monolayer showed that the area/molecule enhanced with increasing mole fraction of **4v** due to strong interaction between **4v**–AA. The isotherms of the mixed films were resulted a shape that practically corresponds to the combination of those of individual components with small differences. The isotherms originated prominent kink points at higher mole fractions of **4v** (0.7, 0.8, 0.9), which corresponded well with that of **4v**. However, this kink point is practically absent at lower mole fractions of **4v** (0.1, 0.3 and 0.5), which was similar to pure AA. Another noticeable feature of the isotherms of **4v**–AA mixed mono-layers is that the isotherms did not converge at higher surface pressures suggesting retain of **4v** in the mixed monolayer between the AA molecules. Thus the DHPM molecules didn't penetrate into the fatty acid monolayer, rather are located underneath the head groups of the densely packed AA monolayer at higher surface pressures. Determination of miscibility in the LB monolayer is very important to understand the basic interactions involved in the DHPM and AA molecules, which are responsible for the stability of the monolayer at the air–water interface. To analyze the degree of miscibility and thermodynamic nature of mixing of the binary components in the mixed LB, we examined the average area per molecule as a function of the film composition at different surface pressures (5, 10, 20, 30, 40 and 45 mN m^{-1}, Fig. 3B). The nature of molecular interactions and also miscibility of the two components were examined by the quantitative analysis of the excess area (A_{E}) of the mixed monolayer at the air–water interface.[14a,b] The excess area was obtained by comparing the experimentally observed average area per molecule (A_{12}) of a mixed monolayer consisting of components 1 and 2 with that of an ideal mixed monolayer (A_{ideal}):

$$A_{\text{ideal}} = A_1N_1 + A_2N_2 \tag{1}$$

where, A_{ideal} is the ideal area per molecule, N_1 and N_2 are the mole fractions of the constituent molecules of the mixed monolayer, A_1 and A_2 are the area per molecule of single component at a fixed surface pressure. The deviation from the ideal behaviour found by computing the excess area of mixing,

$$A_{\text{E}} = A_{12} - A_{\text{ideal}} \tag{2}$$

A_{E} should be zero in the ideal situation.[14a,c] Our **4v**–AA mixed monolayer LB films showed positive deviation from the ideal behaviour at all compositions of the mixtures (Fig. 3B). The results indicate the miscible nature and having repulsive type of interactions between DHPM (**4v**) and AA molecules. The area occupied by the (**4v**–AA) mixed monolayer at a particular surface pressure was greater than the area occupied by the same amount of the pure components, which also supported existence of repulsive interaction between them. The cohesive forces between like molecules **4v**–**4v** and AA–AA dominated in the mixed films with respect to the adhesive force between the unlike components (**4v**–AA) resulting to a partial or total phase separation. It led to formation of aggregated microstructure of **4v** in the mixed films. The photophysical studies[2b,5] of the **4v**–AA mixed, microcrystal and pure **4v** films showed red-shifted and broadened UV-vis spectra (Fig. 3C) in comparison with the pure **4v** in solution (277 nm). The broadening of the spectrum along with the red-shift might be due to formation of J-type of aggregates in the mixed (**4v**–AA) LB films, pure and microcrystal films of **4v**–AA. Interestingly packing pattern of molecules did alter on increasing the mole fraction (0.3, 0.5 and 0.8), which is an important phenomena for technical application of the material. The change in intensity might be due to the change of packing density of **4v** molecules in the mixed LB films. The emission spectrum of **4v** solution (Fig. 3D) showed a peak at 526 nm and a distinct

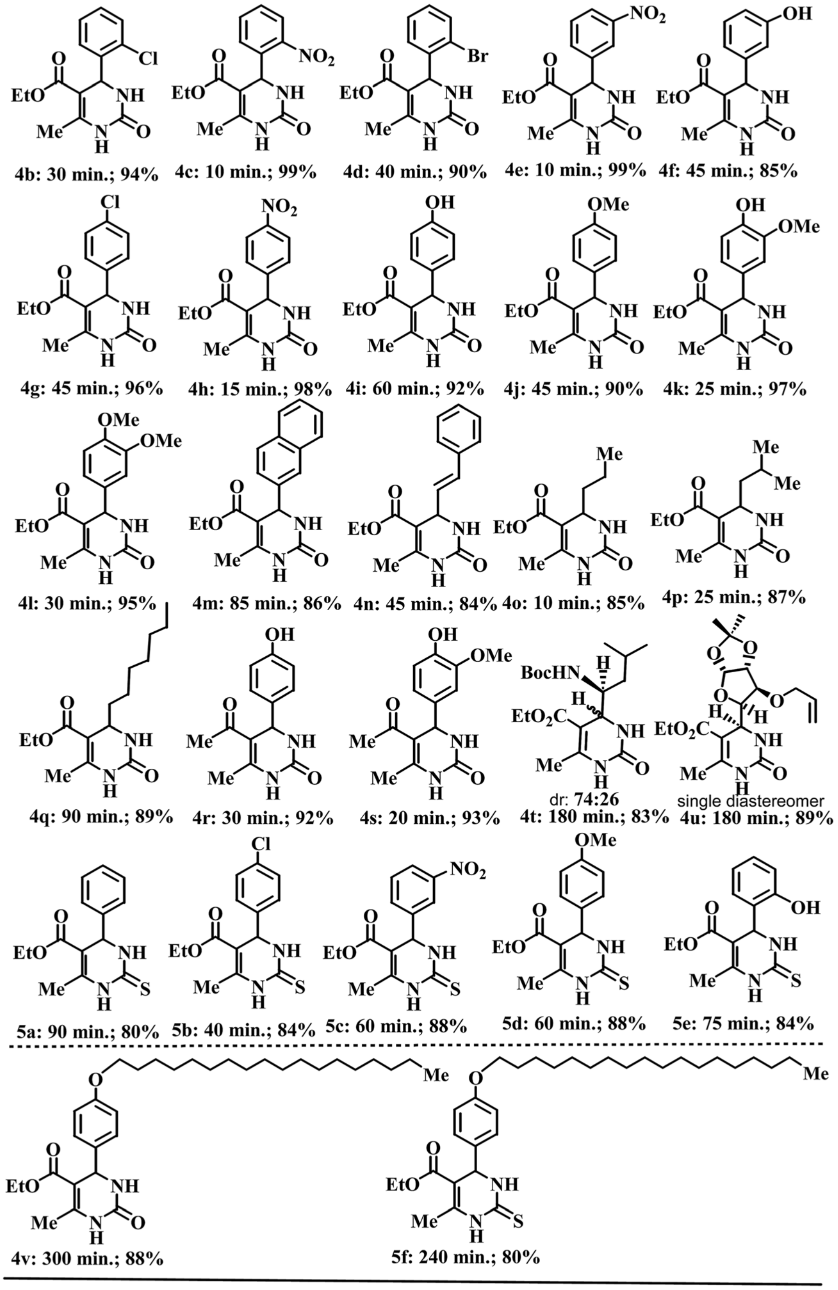


Fig. 2 Synthesized diverse DHPM analogues.

band at 373 nm. The spectra of pure **4v**, microcrystal and mixed film were blue shifted, which were due to a specific orientation and closer association of **4v** in the pure and mixed films.

The AFM imaging[4] of LB monolayer of AA exhibited formation of an aggregated nanowire (panel E, Fig. 3). Similarly, the surface morphology of the pure DHPM (**4v**) monolayer transferred at 25 mN m^{-1} revealed formation of spherical aggregated material of about 100 nm dimension (panel F, Fig. 3). On enhancement of surface pressure to 40 mN m^{-1} changed the packing density of the **4v** monolayer film leading to fabrication of grainy microstructure having a higher density domains (panel G, Fig. 3), which is an outstanding new observation. The AFM image of **4v**–AA mixed LB film (panel H, Fig. 3) established the capability of the DHPM to aggregate with other component leading to construction of organic nanostructures materials, which has tremendous application during fabrication of organic electronic devices.

In conclusion, we have demonstrated a solvent-free, general, IL catalyzed dual C–N/C–C coupled-annulation strategy featuring operational simplicity, atom and energy efficiency, environmental safety, high conversion, fast reaction rate, excellent yield, and tolerance of functionalities and chirality to afford diverse DHPMs, their chiral and marcapto

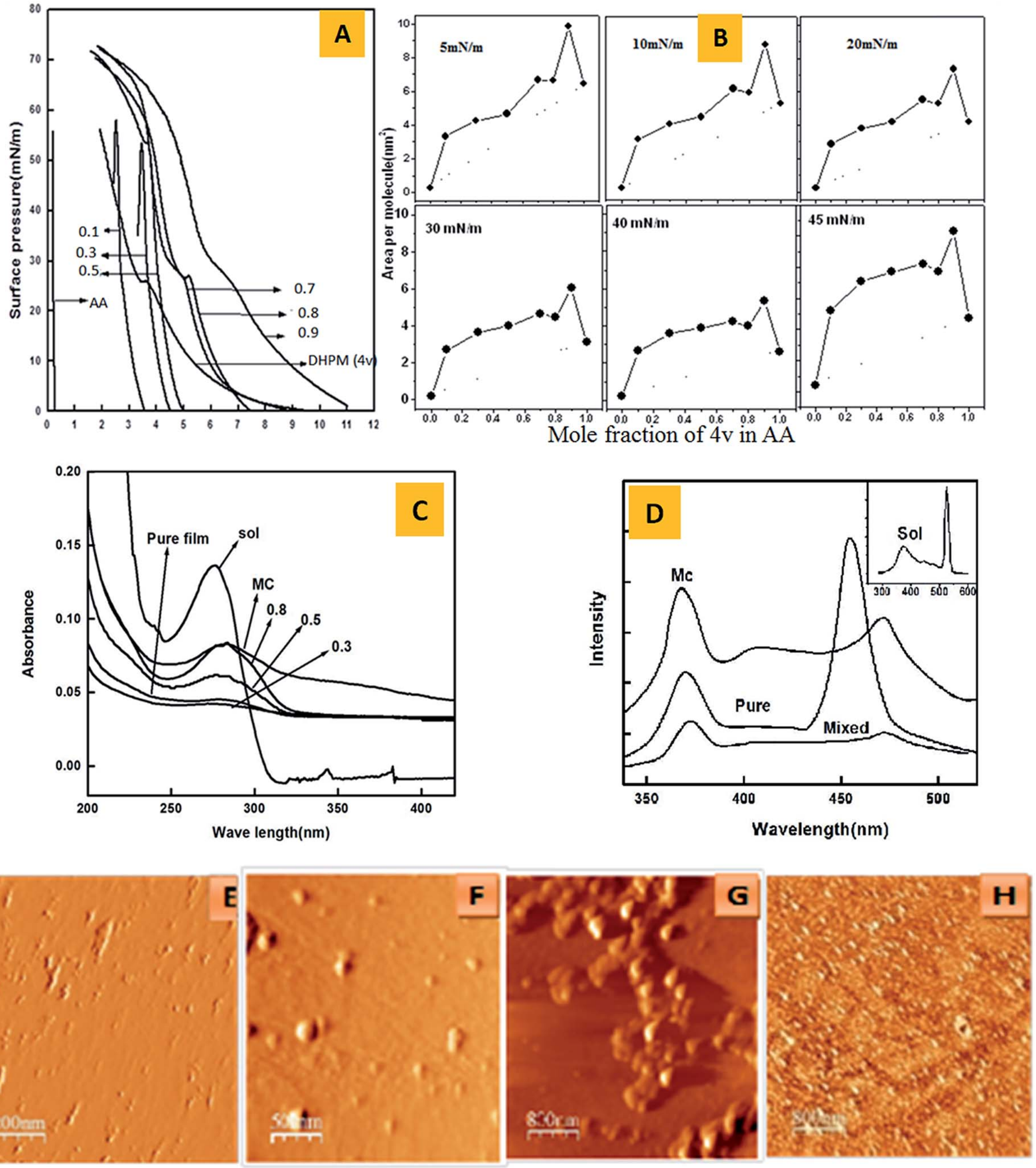


Fig. 3 (A) Surface pressure (*π*) *vs.* area per molecule (*A*) isotherms of mixed monolayers of DHPM (**4v**) and AA at different mole fractions of **4v** along with pure AA and **4v**. (B) Plot of area/molecule *versus* mole fraction for mixed DHPM (**4v**)–AA monolayers on water sub-phase at various surface pressures. (C) UV-vis absorption spectra of DHPM $CHCl_3$ solution (SOL), pure film of **4v** microcrystal (MC) and **4v**–AA mixed LB film at three different mole fractions namely, 0.3, 0.5, 0.8. (D) Emission spectra of DHPM (**4v**) in solution (SOL), **4v** (pure), microcrystal (MC) and **4y**/AA mixed LB film at a mole fraction of 0.5. (E) Atomic force microscope image of monolayer of AA, (F) pure film of DHPM **4v** at 25 mN m^{-1}, (G) pure film of DHPM **4v** at 40 mN m^{-1}, (H) mixed LB film of **4v**–AA.

analogues. In addition, the UV-vis, fluorescence and AFM studies of pure and mixed thin films of the ubiquitous DHPM to innovative futuristic materials for organic electronics, and LB high surface pressure controlled development of outstanding aggregation property will find valuable application in chemical, material and medical sciences.

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