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Thermochromic and highly tunable color emitting bis-tolane based liquid crystal materials for temperature sensing devices



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perature sensing devices.

ARTICLE INFO	A B S T R A C T
Keywords: Luminescent liquid crystals Thermochromic Fluorescence characteristics •	The luminescent compounds based on the D- π -A system consisting of substituted pyrrole as acceptor, π conjugated bis-tolane and -OMe , -N(CH₃)₂ , -N(Ph) ₂ at termini acting as donors have been synthesized. On heating, all the compounds exhibited distinct mesomorphic behavior depending upon donating groups and substituents at the acceptor unit. These luminescent liquid crystals exhibited emission from blue, green to reddish orange with high quantum efficiency in solid as well in solutions state. We discovered the rarely reported three membered ring interactions between the Br at alpha position of pyrrole and acetylene bond and their impact on luminescence efficiency via single crystal structure of 2Br–CN–N(CH₃) ₂ and 2Br–CN–N(Ph) ₂ . Furthermore, the thermochromic behavior of these LLCs compounds has been explored, especially CN–N(Ph) ₂ , its reddish orange emission changed to blue at 240 °C–250 °C in pure state, while in dimethyl silicone polymer (PDMS) film, it switched to blue at 200 °C and completely vanished at 240 °C. These simple and highly emissive compounds display outstanding thermochromic properties above 200 °C. thus will be potentiality valuable for high term-

1. Introduction

Luminescent liquid crystals (LLCs) have numerous potential applications in optoelectronics [1,2] and biomaterials [3–5] due to their unique anisotropic liquid crystalline behavior along with the photophysical characteristics. The LLCs materials might increase the efficiency of the optoelectronic devices by enhancing their features like contrast, brightness and viewing angle [6].

Generally, luminescent liquid crystals are usually constructed by connecting the bis-tolane, tolane or some long molecular segment with the fluorophore. However, the phenomenon of aggregation caused quenching (ACQ) has remained a serious challenge for their applications. So, the development of suitable design, adhering to efficient luminescence became significant field of research. In order to address these challenges, LC mesogens were incorporated to the periphery of AIEs [7,8] to construct highly emissive materials in solid state with liquid crystals characteristics [9–12]. LLCs can be used to develop efficient stimuli responsive materials, as they have tendency to be easily converted into mesophase, so remarkable changes can take place in luminescence intensity or emission color with the phase transition. In 2008, Keto's group described the change of phase from cubic to columnar of pyrene derivative LC, along with the change in emitting color from yellow to blue green at 160 °C [13]. They also reported the couple of liquid crystal phases with emissive color transition from yellow to blue of 2,6-diethynylanthracene derivative on cooling the isotropic phase [14]. In 2012, the Park group reported (2Z,2'Z)-2,2'-(1, 4-phenylene) bis(3-(3,4,5-tris(dodecyloxy)phenyl)acrylonitrile), GDCS, which has no emission in iso-tropic phase, while, on cooling to LC and crystalline state, it exhibited evident green and yellow emission respectively. They also elaborated the role of cyano groups to assist the formation of hexagonal columnar liquid crystal phase at room temperature, which in turn cause the aggregation-induced enhanced emission (AIEE) [15].

Considerable progress has been made for LLCs compounds based on the thermochromism and mechanochromism [16–22]. Most of the LLCs exhibited blue to yellow emissive color [23–26] and to get the red color LLC materials has become focused area of research due to their utilization in sensor and display technology [27,28]. Ionic liquid crystals consisted of thienoviologen fluorophore exhibited the luminescence at 640 nm in nematic columnar phase were reported by Veltri et al. [29]

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https://doi.org/10.1016/j.dyepig.2021.109272

Received 14 February 2021; Received in revised form 24 February 2021; Accepted 25 February 2021 Available online 9 March 2021 0143-7208/© 2021 Elsevier Ltd. All rights reserved.

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Furthermore, electrochromic thienoviologen based ionic LLCs having variable alkyl chain length exhibiting red emission at 630 and 670 nm in columnar and smectic phases respectively have been reported [30,31]. Recently, nitro-substituted pyrrolopyrrole derivative (**TPPP-NO**₂) LCs material having thermochromic and mechano-chromic characteristics has been published. This material started to display red color emission at 135 °C (LC phase), while quenching at 185 °C (isotropic phase) under the turn-on and turn-off mechanism [32].

According to best of our knowledge, until now the published work about thermoresponsive LLC materials indicated the sensing of temperature up to or below to 200 °C. We put an effort to use purely organic luminescent liquid crystals compounds for sensing of high temperature up to 240 °C or more with excellent luminescence efficiency. In this work, we synthesized simple and efficient bis-tolane based luminescent liquid crystals compounds, which exhibited emission from blue to reddish-orange. Our designed molecules are based on D- π -A system, where pyrrole (with or without halogens) containing the –CN group act as withdrawing unit and -**OMe**, -**N**(**CH**₃)₂ and -**N**(**Ph**)₂ at terminal are electron donating groups (Scheme 1).

2. Synthesis

Synthesis of these LLCs is clearly descripted in Scheme 1. Details of the synthesis of the materials are given in the ESI. Compounds CHO-I was synthesized through the methods reported in literature in 75% yield [33]. 2F-CHO-I was synthesized from the reported compound 3, 4-difluoro-1-(4-iodophenyl)-1*H*-pyrrole using Vilsmeier-Haack reaction in 90% yield [34]. Compounds CHO-I and 2F-CHO-I were transformed into the corresponding oxime, further dehydrated with acetic anhydride to give the 1-(4-iodophenyl)-1H-pyrrole-2-carbonitrile (CN-I) and 3, 4-difluoro-1-(4-iodophenyl)-1H-pyrrole-2-carbonitrile (2F-CN-I) [35]. The 1-(4-iodophenyl)-1H-pyrrole-2-carbonitrile (CN-I) was converted to 4,5-dibromo-1-(4-iodophenyl)-1H-pyrrole-2-carbonitrile (2Br-CN-I) using *N*-bromosuccinimide in DMF at 0 °C to room temperature. These three (CN-I, 2F-CN-I and 2Br-CN-I) intermediates were coupled with 1-ethynyl-4-((4-methoxyphenyl)ethynyl)benzene (1c), 4-((4-ethynylphenyl)ethynyl)-N,N-diphenylani -line (2c)and

4-((4-ethynylphenyl)ethynyl)-*N*,*N*-diphenylaniline (3c) to generate corresponding luminescent liquid crystals CN–OMe, CN–N(CH₃)₂, CN–N(Ph)₂, 2Br–CN–OMe, 2Br–CN–N(CH₃)₂, 2Br–CN–N(Ph)₂, 2Br–CN–N(Ph)₂, 2F–CN–OMe, 2F–CN–N(CH₃)₂ and 2F–CN–N(Ph)₂ in 90–96% yield.

3. Photophysical properties

3.1. UV and PL spectra

We studied the absorption and emission properties of the LLCs in DCM (10^{-5} mol/L) as well as in solid state. The spectroscopic data is given in Fig. 1 and summarized photophysical data is given in Table 1. The UV–Vis spectra of the LLCs exhibited the two absorption bands in DCM which is due to the D- π -A system in all the compounds. λ_{abs}^{max} of **CN–OMe, CN–N(CH_3)_2, CN–N(Ph)_2, 2Br–CN–OMe, 2Br–CN–N(CH_3)_2, 2Br–CN–N(Ph)_2, 2F–CN–OMe, 2F–CN–N(CH_3)_2 and 2F–CN–N(Ph)_2 are 333, 368, 376, 333, 371, 378, 334, 371 and 378 nm respectively as shown in Table 1. It is evident that there was no significant difference of \lambda_{abs}^{max} within the compound series containing either -OMe, -N(CH_3)_2** or **-N(Ph)_2** donating groups, while marked difference of about 35–37 nm and 43–44 nm was observed, when **-OMe** group was changed by **-N (CH_3)_2** and **-N(Ph)_2** respectively, which is bathochromic shift due to strong electron donating effect of *N*-dimethylamino and *N*-diphenylamino groups.

The λ_{em}^{max} values in solution form of these **LLCs** as shown in Table 1. There was a slight difference within λ_{em}^{max} values of compounds containing **-OMe** and **-N(Ph)**₂ respectively, while in compounds comprising of **-N(CH_3)**₂, it was more pronounced, about 8–11 nm due to variable positions and electronic cloud of halogens in geometry. Again, the **-N(CH_3)**₂ and **-N(Ph)**₂ groups containing LLCs exhibited remarkable bathochromic shift of about 73–87 nm from their respective methoxy group containing compounds. According to the emission spectra in the solid state, a regular red shift pattern of 6 nm has been observed in **-OMe** containing compounds from **CN–OMe** to **2F–CN–OMe** while variable trend has observed in **-N(CH_3)**₂ containing LLCs. The halogen containing **2Br–CN–N(CH_3)**₂ and **2F–CN–N(CH_3)**₂ exhibited the λ_{em}^{b} at 478 nm and 501 nm while **CN–N(CH_3)**₂ exhibited λ_{em}^{b} at 511 nm. The **-N(Ph)**₂



Scheme 1. Synthesis of Bis-tolane based luminescent liquid crystals (i) 1) NH₂OH.HCl, 2) (AcO)₂O. (ii) NBS, DMF 0 °C, rt. (iii) Pd (PPh₃)₂Cl₂, CuI, Et₃N, CH₃N, 85 °C. (iv) Pd (PPh₃)₂Cl₂, CuI, Et₃N, THF, rt. (v) 1) TMS, Pd (PPh₃)₂Cl₂, CuI, Et₃N, THF, rt. 2) K₂CO₃, MeOH, rt.



Fig. 1. a) Normalized absorption, b) Emission spectra in DCM solution (1×10^{-5} mol/L). c) Photo-luminescence spectra in solid state, Photographs taken under UV illumination d) CN–OMe, e) CN–N(CH₃)₂, f) CN–N(Ph)₂, g) 2Br–CN–OMe, h) 2Br–CN–N(CH₃)₂, i) 2Br–CN–N(Ph)₂, j) 2F–CN–OMe, k) 2F–CN–N(CH₃)₂ and l) 2F–CN–N(Ph)₂.

Table 1

Photophysical data of luminescent liquid crystals compounds.

Compounds	λ _{abs} ^a (nm)	λ _{em} ^a (nm)	Φ _F ^a (%)	λ_{em}^{b} (nm)	Φ _F ^b (%)	$\tau^{\rm b}({\rm ns})$
CN-OMe	333	407	76	455	32	3.60
CN-N(CH ₃) ₂	368	487	89	511	37	5.04
CN-N(Ph)2	376	480	90	627	40	12.7
2Br-CN-OMe	333	411	37	461	6	3.32
2Br-CN-N	371	498	80	478	11	3.63
(CH ₃) ₂						
2Br-CN-N(Ph)2	378	490	89	545	35	5.60
2F-CN-OMe	334	409	68	467	38	4.07
2F-CN-N	371	495	90	501	25	3.09
(CH ₃) ₂						
2F-CN-N(Ph)2	378	488	92	493	36	6.77

 a In DCM (1 \times 10 $^{-5}$ mol/L).

^b Emission data and Absolute quantum yield in solid state.

group containing LLCs exhibited blue shift when we move from nonhalogenated to halogenated LLCs. The halogens exerted the withdrawing effect, but they might have possible interactions with the π -electron of acetylene bonds between the molecules due to that reason, blue shift has been observed in these LLCs and this effect is more evident in case of **2Br–CN–N(CH₃)**₂. The **CN–N(Ph)**₂ exhibited the orange-red emission, having 627 nm λ_{em}^{b} value, which might be due to difference in packing and freely available π -electrons of bis-tolane moiety which made an excellent D- π -A system as compared to respective halogenated LLCs, which displayed emission in green to yellow range.

These LLCs have exhibited excellent quantum efficiency in solution as well as in the solid state. The fluorescence quantum yield in the solution Φ_F^a (%) and solid state Φ_F^b (%) are shown in Table 1. In solutions, quantum efficiency of LLCs containing -N(CH₃)₂ and -N(Ph)₂ is higher due to strong donating effect and relatively strained structure than the compounds with the -OMe donating group. The highest Φ_F^a (%) was exhibited by 2F.

-CN -N(Ph)₂ ($\Phi_F^a = 92\%$) and 2Br–CN–OMe exhibited the lowest ($\Phi_F^a = 37\%$). We measured the absolute quantum yield Φ_F^{b} in calibrated integrating sphere system in solid state. The non-halogenated CN–OMe, CN–N(CH₃)₂ and fluorinated 2F–CN–OMe, 2F–CN–N(CH₃)₂ exhibited good quantum yield, 25%–38%, while brominated, 2Br–CN–OMe and 2Br–CN–N(CH₃)₂ displayed lower Φ_F^{b} , 6% and 11% respectively in powder. All the compounds with the terminal -N(Ph)₂ group exhibited remarkable luminescence efficiency, 35%–40%, which might be due to non-planner structure of terminal diphenyl amino groups to avoid the π - π stacking or severe halogen interactions with the π electrons of bis-tolane system. It is evident from quantum yield data in

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450

340

341

330

Iso

Iso

Iso

Iso

solution and solid state that these luminescent compounds exhibited higher quantum efficiency in solution as compared to solid state due to intermolecular interactions which lower down the luminescence efficiency.

Further, we examined the solvatochromic effect on the λ_{abs}^{max} and λ_{em}^{max} of each compound. In λ_{abs}^{max} of LLCs compound containing **-OMe** donating group, slight blue shift (3–6 nm) has been observed, while the **-N(CH_3)**₂ and **-N(Ph)**₂ containing luminescent compounds exhibited slight blue shift (4–5 nm) and (6–7 nm) respectively, when we move from toluene to polar acetonitrile solvent.

The λ_{em}^{max} values measured in non-polar (toluene) to polar (ACN) solvents have shown irregularity in the pattern. All the **-OMe** and **-N** (**Ph**)₂ containing LLCs, first exhibited red shift when we move from toluene to DCM, then slight blue shift up to THF and then again red shift has been observed. The overall red shift was not remarkable in case of **-OMe**, while compounds containing **-N(Ph**)₂ group displayed red shift of 82–90 nm from toluene to acetonitrile. There was evident bathochromic effect of about 93–104 nm was observed in case of **-N(CH**₃)₂ donating group containing compounds when we move from toluene up to acetonitrile and the highest red shift of about 104 nm was observed in case of **2Br–CN–N(CH**₃)₂. The absorption and emission spectra in different solvents are shown in Figs. S1 and S2 respectively. (See supporting information).

3.2. Thermotropic liquid crystalline property

These bis-tolane based luminescent compounds were able to selfassemble into LC phase upon thermal treatment. The mesophase properties of LLCs were studied by differential scanning calorimetry (DSC) and polarizing optical microscopic (see Fig. 2). The related curves are listed in Figs. S3–S8, corresponding transition temperatures and thermal decom -position temperatures (T_d) were calculated by TGA analysis summarized in Table 2.

From the heat-weight loss curves, the thermal decomposition temperatures of all compounds are above 300 $^\circ C$, which shows good thermal stability.

According to the DSC curves, all the compounds exhibited liquid crystals phases on heating and the compounds with the **-N(CH₃)**₂ terminal group have higher temperature mesophases as compared to compounds containing **-OMe** as terminal group. The polarizing optical microscopy (POM) shows that the **CN–OMe** displayed the Smectic A mesophases, while the bromo and fluoro with the **-OMe** terminal group exhibited the schlieren nematic texture. The nonhalogenated and dibromo compounds with **-N(CH₃)**₂ exhibited texture of Smectic B, while their counterpart, difluoro LLC displayed *mosaic nematic* phase. Interestingly, Smectic A mesophases was observed in case of **CN–N** (**Ph)**₂, while the **2Br–CN–N(Ph)**₂ and **2F–CN–N(Ph)**₂ displayed the

Table 2	
Thermal behavio	r of the LLCs compounds

2Br-CN-N(Ph)2

2F-CN-N(CH₃)₂

2F-CN-N(Ph)2

2F-CN-OMe

Compound	Transition temperatur	Transition temperatures/°C ^a		
CN–OMe	Cr 196 SmA 204	Iso	349	
CN-N(CH ₃) ₂	Cr 239 SmB 244	Iso	347	
CN-N(Ph) ₂	Cr 241 SmA 250	Iso	520	
2BrCNOMe	Cr 204 N 230	Iso	356	
2Br-CN-N(CH ₃) ₂	Cr 272 SmB 284	Iso	357	

Cr 172 SmB 180

Cr 191 SmB 198

Cr 187 N 193

Cr 220 N 226

^a Transition temperature were determined by DSC (peak temperature, first
heating scan, 10 K min $^{-1}$) and confirmed by POM. Cr = crystalline solid, N =
nematic, $SmA = Smectic A$, $SmB = Smectic B$, iso = isotropic liquid state.
^b Decomposition temperature.



Fig. 2. POM texture images of compound a) CN–OMe, b) CN–N(CH₃)₂, c) CN–N(Ph)₂, d) 2Br–CN–OMe, e) 2Br–CN–N(CH₃)₂, f) 2Br–CN–N(CH₃)₂, g) 2F–CN–OMe, h) 2F–CN–N(CH₃)₂ and i) 2F–CN–N(Ph)₂.

Smectic B phase. Furthermore, the temperature ranges of mesophase in nonhalogenated **CN–OMe**, **CN–N(CH₃)**₂ and fluorinated **2F–CN–OMe**, **2F–CN–N(CH₃)**₂ is 6–8 °C, while in case of brominated **2Br–CN–OMe** and **2Br–CN–N(CH₃)**₂, it is 26 °C and 12 °C respectively. In these cases, addition of bromine significantly increased the transition temperature ranges and thermal stability. The LLCs containing the **-N(Ph)**₂ terminal group exhibited the variable behavior and they did not display any separate mesophase peak in DSC. The fluorinated **2F–CN–N(Ph)**₂ and brominated **2Br–CN–N(Ph)**₂ compounds have lower mesophase temperature, melting point and stability as compared to **CN–N(Ph)**₂.

3.3. Thermoresponsive behavior of compound CN-N(Ph)₂

As already mentioned, that the LLCs compounds can be excellent stimulus responsive material and, in this work, we explored the thermoresponsive behavior of bis-tolane based LLCs compounds. Generally, these types of linear compounds display variations in emission intensity rather than remarkable mechanochromism or thermochomism. According to the PL intensity graphs data in Fig. 3 and S12 (Supporting information), the LLCs comprising of $-N(CH_3)_2$ group exhibited green to vellow emissions which converted into the blue emission in their LC phase on heating and same is the case with the 2Br-CN-N(Ph)₂ and 2F-CN-N(Ph)2. We selected the CN-N(Ph)2 LLCs compound as it emitted the orange-red color with broad range of emission and thermodynamically quite stable. The PL intensity regularly decrease with the rise of temperature from 40 $^{\circ}$ C to 200 $^{\circ}$ C with the slight blue shift in the λ_{em}^{max} from 627 nm to 605.6 nm due to change in intermolecular interactions. The emission with 509.6 nm became dominant when we move from 200 °C to 210 °C, which is the green emission. The compound started to exhibit $\lambda_{em}^{max} = 486$ nm at 240 °C and become completely blue at isotropic phase temperature, 250 °C having 478 nm $\lambda_{em}^{max}.$ There was a slight change of 4 nm in wavelength while moving from 241 °C to 250 °C, which was the temperature nearly between the liquid crystal phase and isotropic phase with respect to DSC data. Further, the emission was disappeared when we raised the respect temperature up to 251 °C.

3.4. Thermoresponsive behavior of CN-N(Ph)₂ in PDMS film

As the LC compound **CN–N(Ph)**₂ exhibited the thermochromic behavior, we prepared temperature sensitive film using the Sylgrad 184 (supporting information) and the PL graphs and images of thermoresponsive behavior are given in Fig. 4 and S13 (Supporting information). The CN–N(Ph)₂ in polydimethyl siloxane film exhibited the λ_{em}^{max} value at 622 nm and comparatively different behavior from pure compound. According to Fig. 4 (a, b), while heating from 30 °C to 240 °C, there was no appreciable change in the PL intensity and wavelength up to 90 °C. When we further increased the temperature, the luminescence intensity decreased rapidly with blue shift from 622 nm to 611 nm in λ_{em}^{max} up to 170 °C. Upon further heating up to 190 °C, the λ_{em}^{max} shifted to the 442 nm with the blue emission. The λ_{em}^{max} almost reached to violet region (437 nm) with maximum PL intensity and again started to decrease and completely vanished at 240 °C.

3.5. Crystal structure

As already mentioned that these LLCs exhibited excellent fluorescence features in solid as well as in solvents but quantum yield in DCM solvent is higher as compared to powder form, so to further decipher the solid-state emission behavior, we scrutinized the packing pattern of $2Br-CN-N(CH_3)_2$ (CCDC 2041597) and $2Br-CN-N(Ph)_2$ (CCDC 2057432). The suitable crystals for 2Br-CN-N(CH₃)₂ and 2Br-CN-N (Ph)2 were obtained by slow diffusion of hexane into chloroform, while after several attempts unfortunately we were not successful to get appropriate crystal of CN-N(CH₃)₂ and CN-N(Ph)₂. The 2Br-CN-N (CH₃)₂ and 2Br-CN-N(Ph)₂ both were crystallized out in triclinic system with P-1 space group. In the 2Br-CN-N(CH₃)₂ dihedral angle between pyrrole and aryl ring is 67.16° (Fig. 5a) while in case of 2Br-CN-N(Ph)₂, it was reduced to 59.12° (Fig. 6a) and unit cells of both crystals contain two molecules. (Figs. 5b and 6b). As revealed by the crystallographic data, the bromine at the alpha position of the pyrrole and terminal groups has evident effect in the determination of the packing and luminescence characteristics. There are mainly two types of interactions has been observed in the relatively close packing 2Br-CN-N



Fig. 3. Thermoresponsive behavior of CN–N(Ph)₂ a) Temperature dependent PL Intensity graph b) Normalized PL graph c) Images of compounds during heating process from 30 °C to 250 °C under Uv-light.



Fig. 4. Thermoresponsive behavior of CN–N(Ph)₂ in PDMS film a) Temperature dependent PL Intensity graph b) Normalized PL graph c) Images of thin film during heating process from 40 °C to 240 °C under Uv-light.



Fig. 5. Crystal structures. 2Br-CN-N(CH₃)₂ (CCDC 2041597) a) Top view (dihedral angle), c) side view, and b) packing in unit cell.



Fig. 6. Crystal structure. 2Br-CN-N(Ph)₂ (CCDC 2057432) a) Top view (dihedral angle), c) side view, and b) packing in unit cell.

 $(CH_3)_2$ I) The Br at the alpha position of every single molecule interact with acetylene bond of neighboring molecule, so two such interactions occurred between two molecules. II) The hydrogen on aromatic ring of

one molecule interact with carbon of aromatic ring and again two such interactions existed between two molecules. The interaction of Br with acetylene bond is like three membered. The **2Br–CN–N(Ph)**₂ exhibited

several intermolecular interactions (Fig. 6b) including the hydrogen bonding between the C-HBr and C-H...N in the two-dimensional head to tail packing. In this case Br at the alpha position of one molecule not only formed three-membered ring with the acetylenic bond of another molecule, it also interacted with the electrons of the aromatic ring adjacent to the acetylene bond. Unlike to the 2Br-CN-N(CH₃)₂, It looked like five membered rings containing three triangles and there was only one such interaction existed between two molecules. The Br at beta position of one molecule also interacted with the N of the cyano group of other molecules in head to head parallel interactions. In the 2Br-CN-N(Ph)2, the terminal non-planar diphenyl group also exhibited weak intermolecular interactions and played significant role in relatively slipped packing which was minor in case of dimethylamino in 2Br-CN-N(CH₃)₂. The molecules of 2Br-CN-N(Ph)₂ have relatively more bent geometry than the 2Br-CN-N(CH₃)₂, rather the linear in typical head to tail packing. So, the excessive weak intermolecular forces, the relatively strained and bent structure made the 2Br-CN-N (Ph)₂ highly emissive as compared to 2Br-CN-N(CH₃)₂. Additionally, the dislocated two-dimensional head to tail lose packing avoided the significant π - π stacking ensured the high fluorescence quantum yield in solid state.

3.6. Theoretical calculations

The structural optimization and frequency operations were conducted under density functional theory (DFT) with Gaussian 09 software by using the parameters B3LYP/6-311G in gas phase for better understanding of electrochemical properties. As shown in Fig. S14 (supporting information), the electronic density in HOMOs of all compounds is mainly localized in the bis-tolane tail, specifically in cases compounds comprising the -N(CH₃)₂ and -N(Ph)₂ donating group at terminal. The LUMOs of these LLCs exhibited almost uniform distribution of electron density over the whole molecules, except the 2Br-CN-OMe and 2Br-CN-N(CH₃)₂, where the electron density is mainly contained on the bis-tolane central core. There is appreciable effect on the dipole moment (D) and Eg (eV) values of these LLCs has been observed by varying the weak H to strong F electronegative atoms on the pyrrole along with the CN group as well as from weak -OMe to strong electron donating terminal group -N(CH₃)₂. As shown in Table 3, dipole moment value of CN-OMe and CN-N(Ph)2 is 4.641871(D), 5.393223 (D) respectively while their counterpart CN-N(CH₃)₂ has dipole moment 7.541696 (D), so introduction of strong electron-donor at the terminal increase the dipole moment value in each case on this D- π -A bis-tolane conjugated system. Likewise, 2F-CN-N(CH₃)₂ exhibited 11.234129 (D), highest value of dipole moment due to most electronegativity fluorine atoms on pyrrole ring as withdrawing groups. The ΔE (eV) values decreases when we move from weak to strong electron-donor at terminal in each case as well as from weak to strong electronegative substituents at pyrrole ring. The LLCs with -N(Ph)₂ donor terminal group exhibited the lowest HOMO LUMO energy gap difference among their counter parts which might be one of reason for their better quantum efficiency.

4. Conclusion

We have synthesized the bis-tolane based luminescent liquid crystals with highly tuneable photophysical characteristics. These LLCs exhibited from blue to orange-red emission with high quantum efficiency in solid state as well in solutions. We comparitively studied the effect of halogens and different terminal substituents on the photophysical properties of these D- π -A based LLCs. All the compounds with -**OMe** and -**N(CH₃)**₂ donor terminal groups displyed blue and green color respectively with high quantum efficiency in solid state except the bromo substituted compounds. The fluorinated and brominated compounds with -**N(Ph)**₂ donor group exhibited green and near to yellow emission color, while **CN–N(Ph)**₂ exhibited orange-red emission with 627 nm of $\lambda_{\text{em}}^{\text{max}}$ with excellent quantum efficiency. The same crystalline system of

Table 3

HOMO, LUMO, I	Dipole Moment	(D) and ΔE	values of LLCs.
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Compounds	HOMO (eV)	LUMO (eV)	Dipole Moment (D)	E _g (eV)
CN-OMe	-5.65	-2.08	4.641871	3.57
CN-N(CH ₃) ₂	-5.13	-1.93	7.541696	3.20
CN-N(Ph) ₂	-5.24	-2.10	5.393223	3.14
2Br-CN-OMe	-5.73	-2.19	5.576457	3.54
2Br-CN-N(CH ₃) ₂	-5.19	-2.05	8.570052	3.14
2Br-CN-N(Ph)2	-5.28	-2.21	5.796434	3.07
2F-CN-OMe	-5.76	-2.28	8.771031	3.48
2F-CN-N(CH ₃) ₂	-5.21	-2.15	11.234129	3.07
2F-CN-N(Ph) ₂	-5.29	-2.29	8.555128	3.00

2Br–CN–N(NH₃)₂ and **2Br–CN–N(Ph)**₂ carring the three membered type of alpha Br bonding interaction with acetylene electrons exhibiting different quantum efficiency have been firstly explored. The **CN–N(Ph)**₂ exhibited excellent thermochromic behavior while heating near to LC phase from 240 °C to 250 °C in pure state. The thin film of PDMS mixed with **CN–N(Ph)**₂ displayed evident color switching from orange to greenish blue at 190 °C, which turn to completely blue at 200 °C and turn off phenomenon at 240 °C. These compounds display excellent high temperature luminescence & mesophase behavior and have potential to be used in temperature sensor devices as these thermochromic changes are visible under naked eye.

Majeed Irfan: Investigation, Resources, Methodology, Data curation, Writing – original draft, Formal analysis, Sumra Idrees: Resources, Mei Zhang: Resources, Zicun Song: Resources, Tingting Liu: Project administration, Funding acquisition, Supervision. Zhuo Zeng: Project administration, Funding acquisition, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors gratefully acknowledge the support of Science and Technology Planning Project of Guangdong Province (2017A010103017), National Natural Science Foundation of China (51703069, 21272080), Special Innovation Projects of Common Universities in Guangdong Province (20178S0182).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109272.

References

- Tong J, Wang YJ, Wang Z, Sun JZ, Tang BZ. Crystallization-induced emission enhancement of a simple tolane-based mesogenic luminogen. J Phys Chem C 2015; 119:21875–81.
- [2] Gupta RK, Pradhan B, Pathak SK, Gupta M, Pal SK, Ammathnadu Sudhakar A. Perylo [1, 12-b, c, d] thiophene tetraesters: a new class of luminescent columnar liquid crystals. Langmuir 2015;31:8092–100.
- [3] Fink TD, Zha RH. Silk and silk-like supramolecular materials. Macromol Rapid Commun 2018;39:1700834.
- [4] Liu K, Zheng L, Ma C, Göstl R, Herrmann A. DNA-surfactant complexes: selfassembly properties and applications. Chem Soc Rev 2017;46:5147–72.
- [5] Yamada S, Morita M, Agou T, Kubota T, Ichikawa T, Konno T. Thermorespon- sive luminescence properties of polyfluorinated bistolane-type light-emitting liquid crystals. Org Biomol Chem 2018;16:5609–17.
- [6] Mei J, Leung NLC, Kwok RTK, Lam JWY, Tang BZ. Aggregation-induced emission : together we shine, united we soar! Chem Rev 2015;115:11718–940.
- [7] Luo J, Xie Z, Lam JWY, Cheng L, Chen H, Qiu C, et al. Aggregation-induced emission of 1-methyl-1, 2, 3, 4, 5-pentaphenylsilole. Chem Commun 2001:1740–1.
- [8] Yang J, Chi Z, Zhu W, Tang BZ, Li Z. Aggregation-induced emission: a coming-ofage ceremony at the age of eighteen. Sci China Chem 2019;62:1090–8.

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- [9] Kim J, Cho S, Cho B. An unusual stacking transformation in liquid-crystalline columnar assemblies of clicked molecular propellers with tunable light emissions. Chem Eur J 2014;20:12734–9.
- [10] Liu Y, You LH, Lin FX, Fu K, Yuan WZ, Chen E-Q, et al. Highly efficient luminescent liquid crystal with aggregation-induced energy transfer. ACS Appl Mater Interfaces 2018;11:3516–23.
- [11] Yuan WZ, Yu Z-Q, Lu P, Deng C, Lam JWY, Wang Z, et al. High efficiency luminescent liquid crystal: aggregation-induced emission strategy and biaxially oriented mesomorphic structure. J Mater Chem 2012;22:3323–6.
- [12] Zhao D, Fan F, Cheng J, Zhang Y, Wong KS, Chigrinov VG, et al. Light-emitting liquid crystal displays based on an aggregation-induced emission luminogen. Adv Opt Mater 2015;3:199–202.
- [13] Sagara Y, Kato T. Stimuli-responsive luminescent liquid crystals: change of photoluminescent colors triggered by a shear-induced phase transition. Angew Chem 2008;120:5253–6.
- [14] Sagara Y, Yamane S, Mutai T, Araki K, Kato T. A stimuli-responsive, photoluminescent, anthracene-based liquid crystal: emission color determined by thermal and mechanical processes. Adv Funct Mater 2009;19:1869–75.
- [15] Yoon S, Kim JH, Kim KS, Chung JW, Heinrich B, Mathevet F, et al. Mesomorphic organization and thermochromic luminescence of dicyanodistyryl- benzene-based phasmidic molecular disks: uniaxially aligned hexagonal columnar liquid crystals at room temperature with enhanced fluorescence emission and semiconductivity. Adv Funct Mater 2012;22:61–9.
- [16] Lehmann M, Gloza S, Roth S. At the limits of liquid crystallinity: stimuli responsive 3d columnar liquid crystals and soft crystals of supramolecular anthracene mesogens. Chem Mater 2015;27:8181-4.
- [17] Mitani M, Ogata S, Yamane S, Yoshio M, Hasegawa M, Kato T. Mechanoresponsive liquid crystals exhibiting reversible luminescent color changes at ambient temperature. J Mater Chem C 2016;4:2752–60.
- [18] Sagara Y, Weder C, Tamaoki N. Asymmetric cyclophanes permit access to supercooled nematic liquid crystals with stimulus-responsive luminescence. Chem Mater 2017;29:6145–52.
- [19] Akamatsu N, Hisano K, Tatsumi R, Aizawa M, Barrett CJ, Shishido A. Thermo-, photo-, and mechano-responsive liquid crystal networks enable tunable photonic crystals. Soft Matter 2017;13:7486–91.
- [20] Sol JAHP, Dehm V, Hecht R, Würthner F, Schenning APHJ, Debije MG. Temperature-responsive luminescent solar concentrators: tuning energy transfer in a liquid crystalline matrix. Angew Chem Int Ed 2018;57:1030–3.
- [21] Zhang P, Kragt AJJ, Schenning APHJ, de Haan LT, Zhou G. An easily coatable temperature responsive cholesteric liquid crystal oligomer for making structural colour patterns. J Mater Chem C 2018;6:7184–7.

- [22] Mu B, Quan X, Zhao Y, Li X, Tian W. Fluorophore core-engineered supra-molecular discotic columnar liquid crystals with tunable fluorescent behavior. Mater Chem Front 2019;3:1671–7.
- [23] Li L, Salamończyk M, Shadpour S, Zhu C, Jákli A, Hegmann T. An unusual type of polymorphism in a liquid crystal. Nat Commun 2018;9:1–8.
- [24] Hiscock LK, Raycraft BM, Wałesa-Chorab M, Cambe C, Malinge A, Skene WG, et al. Synthesis and characterization of liquid-crystalline tetraoxapentacene deri -vatives exhibiting aggregation-induced emission. Chem Eur J 2019;25:1018–28.
- [25] Guo L-X, Xing Y-B, Wang M, Sun Y, Zhang X-Q, Lin B-P, et al. Luminescent liquid crystals bearing an aggregation-induced emission active tetraphenylthio- phene fluorophore. J Mater Chem C 2019;7:4828–37.
- [26] Song F, Cheng Y, Liu Q, Qiu Z, Lam JWY, Lin L, et al. Tunable circularly polarized luminescence from molecular assemblies of chiral AIEgens. Mater Chem Front 2019;3:1768–78.
- [27] Zhao D, He H, Gu X, Guo L, Wong KS, Lam JWY, et al. Circularly polarized luminescence and a reflective photoluminescent chiral nematic liquid crystal display based on an aggregation-induced emission luminogen. Adv Opt Mater 2016;4:534–9.
- [28] Zhao D, Fan F, Chigrinov VG, Kwok HS, Tang BZ. Aggregate-induced emission in light-emitting liquid crystal display technology. J Soc Inf Disp 2015;23:218–22.
- [29] Veltri L, Maltese V, Auriemma F, Santillo C, Cospito S, La Deda M, et al. Mesoph -ase tuning in discotic dimers π-conjugated ionic liquid crystals through supramolecular interactions and the thermal history. Cryst Growth Des 2016;16: 5646–56.
- [30] Beneduci A, Cospito S, La Deda M, Veltri L, Chidichimo G. Electrofluoro- chromism in π-conjugated ionic liquid crystals. Nat Commun 2014;5:1–8.
- [31] Beneduci A, Cospito S, Deda M La, Chidichimo G. Highly fluorescent thienoviolo -gen-based polymer gels for single layer electrofluorochromic devices. Adv Funct Mater 2015;25:1240–7.
- [32] Dai S, Zhou Y, Zhang H, Cai Z, Tong B, Shi J, et al. Turn-on and color-switchable red luminescent liquid crystals based on pyrrolopyrrole derivatives. J Mater Chem C 2020;8:11177–84.
- [33] Xu Z-L, Li H-X, Ren Z-G, Du W-Y, Xu W-C, Lang J-P. Cu (OAc) 2[•] H₂O-cataly-zed Narylation of nitrogen-containing heterocycles. Tetrahedron 2011;67:5282–8.
- [34] Bu X, Zhu D, Liu T, Li Y, Cai S, Wang H, et al. Approach to tuned emitting color of luminescent liquid crystals with substituted fluoropyrrole acceptor unit. Dyes Pigments 2017;145:324–30.
- [35] Zhang M, Bu X, Liu T, Guo W, Wang H, Zeng Z. Adjustable 2-cyano-3, 4-difluoro-1H-pyrrole-based luminescent liquid crystals: synthesis, properties and substituent effect. J Mol Liq 2018;264:425–30.