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# Exceptional dual fluorescent, excited-state intramolecular proton-transfer (ESIPT) columnar liquid crystals characterized by J-stacking and large Stokes shifts



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# ABSTRACT

Excited-State Intramolecular Proton-Transfer (ESIPT) fluorophores are emerging as promising future materials for electronic and biotechnological applications. ESIPT columnar (Col) liquid crystals (LCs) have been especially projected as the apt materials for advanced technological endeavors. But, there are hardly any explorations in this direction and thus, needing immediate attention. Herein we report on the synthesis, characterization, and ESIPT activity of a homologous series of novel phasmidic bis(N-salicylideneaniline) Col LCs. Optical microscopic, calorimetric and powder X-ray diffraction (XRD) studies evidence the occurrence of hexagonal columnar (Col<sub>h</sub>) phase having p6mm symmetry where the constituent slices result from the self-assembly of a pair of mesogens in a side-by-side manner facilitated by intense longitudinal  $\pi$ - $\pi$  interactions. X-ray data confirm the absence of both directionally correlated tilting of the slices and transverse core-core interactions within the columns. Fluorescence probing clearly evidence the ESIPT occurring not only in DCM solution of the mesogens but also in their three-condensed states viz., solid, liquid crystal, and isotropic liquid phase; in general, two archetypal emission bands at ~430 nm (weak) and ~ 630 nm (strong) with large Stokes shifts (250-275 nm) of ESIPT phenomenon have been observed. The slow shift of emission maxima of the ESIPT fluorescence as a function of decreasing temperature without photoluminescence quenching coupled with the estimated tilt angle ( $\Theta$ ) of the slices normal to the columnar axis (37 to 42°), from the XRD data, confirm the formation of so-called Scheibe or J-aggregates. The redox activity, metal ion sensing ability, and solvatochromism of the mesogens have also been investigated. The study suggests that these ESIPT Col LCs with band-gap of about 3 eV can be regarded as wide-bandgap semiconducting materials having the electronic characteristics falling between those of conventional semiconductors and insulators.

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# 1. Introduction

Functional materials belong to a special class of man-made substances that are mostly organic or inorganic or hybrid/composite substances ranging from small molecular (low molar mass) compounds to polymers. [1–9] They, being hard [1–8] or soft [9] in nature, possess the ability to display predetermined physicochemical properties/phenomenon under the influence of an external stimulus such as light, temperature, sound, electric field, magnetic field, mechanical stress, substrate surface anchoring conditions, etc. Among wide varieties of soft functional materials reported hitherto, liquid crystals (LCs) have secured a prominent position in materials science encompassing the aspects of both basic research and applied science. [10–12] They are self-organized fluid (soft) superstructures and thus, possess the inherent ability of not only responding to the aforesaid external stimuli but

\* Corresponding author. *E-mail address:* yelamaggad@cens.res.in (C.V. Yelamaggad). also structural defect eliminating property through the natural selfhealing process. It has been well demonstrated over the years that the exceptional characteristics of LCs, which were so far associated mainly with the LC display technology, can be well-exploited in devices such as semiconductors, sensors, elastomer actuators, photovoltaics, organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), etc. [11,13,14]

For example, such technological endeavors are attainable by utilizing the exceptional characteristics of columnar (Col) LC phases formed by the parallel packing of infinitely long columns organized in twodimensional (2D) lattices; their intrinsic electronic features originate purely from the disk-like (discotic) aromatic or heteroaromatic cores, substituted peripherally with three to several flexible aliphatic tails, stacked co-facially in columns through intense  $\pi$ - $\pi$  associations/interactions. [15–21] While the insulating alkyl chains prevent the closer intercolumnar interactions, the  $\pi$ - $\pi$  interaction of discotic mesogens in each column creates 1D charge carrier pathway along the long column axis. The average  $\pi$ - $\pi$  stacking distance of the discotic cores in a column is typically of the order of 3.5 Å, and thus, an overlap of the  $\pi$ - $\pi$ \* lowest unoccupied molecular orbitals (LUMOs) should be possible. [16,17,21] Thus, the Col phases, which have been aptly regarded as molecular wires or quasi-one-dimensional (Q1D) conductors, hold huge promise for the field of organic electronics due to their intrinsic ability to serve as the active media, in the form of thin-films, to perform the essential functions such as carrier-injection or blocking, and electron-hole recombination or separation. [16-21] However, in recent years, considerable efforts have been devoted not only to control the vital parameters such as oxidation potential and electron affinity but also to incorporate the light absorption and luminescent properties to enable Col phase to serve as the emissive layers. [16-22] Thus, fluorescent Col LCs have not only the ability to replace light-emitting amorphous/crystalline solids [23-25] but also possess promising technological aspects such as long-range order [16], charge-transport property / anisotropic conductivity, [16,19,26] long exciton diffusion lengths, [27,28] self-healing ability [16,17], low-cost solution processability [16] etc. The Col phases are generally classified, depending upon the degree of order in the molecular stacking, the alignment of the discogens along the columnar axis, and the symmetry of the 2D lattice, into seven different classes. Of these, Col hexagonal (Col<sub>b</sub>) and/or Col rectangular (Col<sub>r</sub>) phases are often encountered in many discotic LCs. [16,17] While four different lattice symmetries viz., p2mm, c2mm, p2gg, and p2mg are assigned for the Col<sub>r</sub> phase, the Col<sub>b</sub> phase, wherein the columns are arranged on a 2Dhexagonal lattice, is generally described by the plane group *p6mm*. [16]

As is well known, a special type of Col<sub>b</sub> phase is formed by the selfassembly of simple non-discoid LCs, called phasmidic or polycatenar mesogens. They comprise a long rod-like core ending on either side with lipophilic segments comprising two or three flexible tails. [12,16,29-44] They have been categorized according to the total number of *n*-alkoxy tails they possess; for example, polycatenars substituted with four, five and six terminal paraffinic tails have been respectively referred to as tetracatenars, pentacatenars and hexacatenars [29–32]. These relatively new class of thermotropic LCs bridge the gap between conventional rod-like and disk-shaped LC molecular architectures, and thus, they exhibit a rich polymesomorphism. That is, experimentally, it has been evidenced that these hybrid mesogens not only show the nematic (N), smectic (lamellar) as well as bicontinuous/micellar cubic, tetragonal and orthorhombic three-dimensional phases but also stabilize a unique Col<sub>b</sub> phase in a series of compounds or pure material. [12,16,29-33] However, such phase transitional behavior largely depends on the number of alkoxy tails they possess on either side of the central calamitic core. Of the variety of polycatenar LCs reported hitherto, the hexacatenars (phasmids) have been attracting attention not only because of their inherent ability to self-assemble into Col phase but also they provide the opportunity to incorporate functional characteristics through the selection of predetermined molecular structural segments. Thus, a wide variety of functional phasmids have been realized, which include heterocycles, [33-38] metallomesogens, [38] ionic LCs, [40,41] photo-responsive mesogens, [42] intra-molecular Hbonded systems, [43,44] thermochromic LCs, [45] bent-core compounds, [46,47] fluorescent materials etc. [48-64]

However, the fluorescent phasmidics, owing to their technological relevance, have been studied intensively through the rational design and synthesis of diverse series of materials derived from functional fluorophores [48–65]. Of these, there has been a thought-provoking work by Park and co-workers reporting that phasmidic LCs, possessing intra-molecular proton-transfer (ESIPT) activity, form tilted (*J*-type) stacking in the column of the LC phases; interestingly, this assembly augments the fluorescence emission of the mesophase with a quantum yield of 34% and a large Stokes' shift (173 nm) [65]. It is speculated that the ESIPT fluorescence coupled with Col behavior make the phasmidics ideal candidates for applications in emissive LCDs, polarized organic lasers and anisotropic OLEDs. [34,65] Thus, we became interested in working on this topic of research and accordingly, searched for the ESIPT active molecules for incorporating Col mesomorphic behavior.

Among the various types of ESIPT active molecules reported hitherto, [43,44,66–73] salicylideneanilines attracted our attention owing to their potential for various technological endeavors. [67] In particular, the investigations on phasmidic LCs by Hiremath [43,44] clearly hinted that the mesomoprism can be induced in bis(*N*-salicylideneaniline)s (BSANs). It was observed in this detailed study that out of the three constitutional isomeric bis(N-salicylideneaniline)s, viz., BSAN-I, BSAN-II & BSAN-III (Fig. 1), the isomers belonging to BSAN-I category derived from 3,6-diformylcatechol shows columnar behavior. These conformers (BSAN-I) can undergo a reversible proton-transfer process to furnish two tautomers, namely, enol-imine (OH) (BSAN-I(OH)), and ketoenamine (NH) (BSAN-I(NH)) forms (Fig. 1). That is, these compounds have the intrinsic ability to display ESIPT fluorescence owing to their novel structural composition where the intramolecular hydrogen (H)bonding correlation among a hydrogen bond donor (-OH) group and a hydrogen bond acceptor (-C=N, imine) linking group exists. Despite these exciting feature, the investigations on the photophysical properties of BSAN-I columnar LCs have not been revealed hitherto. Thus, we set out our goal to realize the analogs of BSAN-I hexacatenars and evaluate their ESIPT activity. Herein, we report on the synthesis and detailed characterization of a series of ESIPT active phasmidic bis(Nsalicylideneaniline)s (PBSANs) existing in Enol-Imine form, which upon photoexcitation transforms into Keto-Enamaine tautomeric form (Fig. 1).

# 2. Results and discussion

## 2.1. Synthesis and characterization

The conventional synthetic steps employed for the preparation of target PBSAN materials have been outlined in Scheme 1. Gallic acid was treated with ethanol in the presence of an acid catalyst to obtain ethylgallate (1) [51], which was subjected to O-alkylation with *n*-alkylbromides under the reaction conditions of Williamson ether synthesis protocol to get ethyl 3,4,5-tris(n-alkyloxy)benzoates (2a-j) [52]. Alkaline hydrolysis of esters 2a-j using aqueous sodium hydroxide (5%) in ethanol provided the corresponding 3,4,5-tris (*n*-alkyloxy)benzoic acids (**3a-i**) [53] which were esterfied with 4nitrophenol in the presence of N,N'-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) to obtain 4-nitrophenyl 3,4,5-tris(*n*-alkyloxy)benzoates (4a-j) [53]. Hydrogenation of these nitro compounds **4a-i** in the presence of Pd—C (10%) and under hydrogen (H<sub>2</sub>) balloon (1 atm) conditions afforded 4-aminophenyl 3,4,5-tris (*n*-alkyloxy)benzoates (**5a-i**) [54]. The central core of the target phasmids namely 2,3-dihydroxyterephthalaldehyde (7) was synthesized starting from 1,2-dimethoxybenzene. It was subjected to lithiation using n-butyllithium (n-BuLi) in the presence of tetramethylethylenediamine (TMEDA), and the treatment of mettallated intermediate with N, N-dimethylformamide (DMF) yielded 2,3-dimethoxyterephthalaldehyde (6). [55]

O-Demethylation facilitated by boron tribromide (BBr<sub>3</sub>) of compound **6** afforded the vital intermediate **7**. [56,57] Finally, an acidcatalyzed condensation of amines (**5a-j**) with aldehyde **7** afforded the desired materials in good yields (69–75%). The molecular structures of all synthesized liquid crystals were ascertained unambiguously using the data derived from spectroscopic techniques viz., UV–visible, FTIR, <sup>1</sup>H NMR & <sup>13</sup>C NMR, see Figs. S3 to S20 of supporting information (SI), and elemental analyses. These characterization data, along with the synthetic procedure of these final mesogens, are given in the experimental section (II.5). However, the intermediates, **2a-j**, **3a-j**, **4a-j**, **5a-j**, **6** & **7**, accomplished here are known compounds <sup>51–57</sup>. and they have been examined for their molecular structures with the aid of FTIR, <sup>1</sup>H NMR, and elemental analyses only. The synthetic procedures and characterization data of these precursors have been presented in supporting information (SI).



BSANs-I(OH): Enol-Imine (OH) form **BSANs-I** :  $R_1 = R_2 = R_3 = OC_nH_{2n+1}$ ; n = 8 & 10



BSANs-I(NH): Keto-Enamine (NH) form



**BSANs-II**:  $R_1 = R_2 = R_3 = OC_nH_{2n+1}$ ; n = 8 & 10



**BSANs-III**:  $R_1 = R_2 = R_3 = OC_nH_{2n+1}$ ; n = 8 & 10



Fig. 1. Skeletal structures of the previously studied hexacatenar LCs (BSAN-I, II & III; Refs. 43 & 44) - the source of present work. Structures of the phasmidic bis(N-salicylideneaniline)s, (PBSANs) investigated in the present work.

## 2.2. Thermal properties and mesomorphic behavior

The thermal and mesomorphic properties of the newly synthesized PBSAN materials were evaluated by a combination of polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and variable-temperature X-ray diffraction (XRD). To figure out the phase transitions/temperatures, a minute quantity (~1 mg) of the pristine sample, held between a glass slide and a coverslip, was subjected to repeated heating-cooling scans using a hot stage and viewed under POM. DSC thermograms for the heating-cooling scans of the mesogens were recorded at a rate of 5 °C / min to confirm the transition temperatures and enthalpy changes of phase transitions. The data derived from these studies are given in Table 1. It is apparent from the collected data that the first (lowest) member of the series is non-mesomorphic, whereas the remaining members are liquid crystalline exhibiting an identical, thermodynamically stable mesophase. Upon heating, the pristine samples PBSAN-6 to PBSAN-12, PBSAN-14 and PBSAN-16 undergo an endothermic phase transition from solid to mesomorphic state,

characteristically displaying a fluid and homogeneous birefringent texture that remains unaltered until the isotropization temperature. The fluidity of the phase was evident from the fact that the coverslip of the specimen could be moved with great ease using a pair of tongue or a paper pin. Upon cooling, a transition from the isotropic liquid state into mesophase occurs, with the texture showing typical defects associated with the Col<sub>h</sub> phase.

The optical texture of the Col phase appears to vary notably from one homolog to another. For example, as shown in Figs. 2a-c, the POM textures of the Col phase formed by mesogens PBSAN-10, PBSAN-11, and PBSAN-14 differ considerably from each other. The texture of the Col phase, emanating from the dark background of isotropic liquid of compound **PBSAN-10**, appears initially as tiny batonnets that eventually coalesces to a pseudo focal-conic fan-like texture as shown in Fig. 2a. The Col phases formed while cooling from the isotropic phase of PBSAN-11 and PBSAN-14 exhibit pseudo-isotropic (homeotropic) texture, respectively comprising linear birefringent defects (Fig. 2b) and flower-like texture/spherulitic domains (Fig. 2c). However, some of



### Scheme 1.

the phasmids displayed uniform (dark) domain of homeotropically aligned Col<sub>b</sub> phase where column axes are vertical to the glass surface; this is notable given the fact that the homeotropic alignment of Col phase can be used in solar cells or OLEDs. Needless to say, the large homeotropic domains appearing dark under POM reveal that these LC phases are optically uniaxial, which is typical for the Colh phase. Thus, the Col phase formed by these compounds remains unaltered nearly up to room temperature (RT), and eventually, it transforms into a solid-state with an exception for the member PBSAN-9 where the Col phase freezes (Table 1 & Fig. S21). The phase transitions and the corresponding temperatures were found to be highly reproducible for any number of heating/cooling scans during POM study, implying that the synthesized phasmids possess excellent thermal stability and hydrolytic resistance. Fig. 3a and b depict the representative DSC traces obtained respectively for PBSAN-9 and PBSAN-14 where the peak positions of the Col-I/I-Col phase transitions of the two consecutive heating-cooling scans remain almost unaffected. Thus, as envisaged,

DSC profiles of the LCs corroborate the inference described above of the POM study.

The indication from the POM textural investigations that the newly prepared phasmidic LCs exhibit a columnar hexagonal phase was substantiated with variable-temperature powder X-ray diffraction (XRD) experiments. XRD patterns were obtained for three compounds viz., **PBSAN-11**, **PBSAN-12**, and **PBSAN-14** as representative cases. The samples were heated to their isotropic liquid state and filled into capillary tubes (1 mm) of Lindemann glass. They were cooled into the Col phase at a rate of 5 °C / min, and the diffraction patterns of the LC phase were recorded at two different temperatures for each selected sample. Figs. 4a, S22 & 4b respectively portray the 1D intensity vs diffraction angle (2 $\theta$ ) profiles of mesogens **PBSAN-11**, **PBSAN-12**, and **PBSAN-14**. Table 2 provides the Bragg reflections along with the results pertaining to the detailed indexation of the mesophases of each phasmid LC. It is thus evident from the XRD patterns (Figs. 4a-b & S22) and the corresponding data collected in Table 2 that compounds

Phase transition temperatures (°C)<sup>a</sup> and associated enthalpies (kJ/mol) of transitions obtained for the phasmidic mesogens of **PBSAN**–*n* series, Cr: Crystal; Col<sub>h</sub>/*p6mm*: Hexagonal columnar phase having *p6mm* symmetry; 1: isotropic liquid state.

LCs	Phase sequence				
	Heating; Cooling				
PBSAN-5	Cr 151.7 (41.9) I; I 114 (1.27) Cr				
PBSAN-6	Cr 112.9 (3.1) Col <sub>h</sub> /p6mm 118.9 (1.6) l; l 114.5 (1.5) Col <sub>h</sub> /p6mm 61.8 (3.18) Cr				
PBSAN-7	Cr 61.8 (3.9) Col <sub>h</sub> /p6mm 120 (1.6) I; I 116.4 (1.5) Col <sub>h</sub> /p6mm 44.0 (0.2) Cr				
PBSAN-8	Cr 55.8 (5.5) Col <sub>h</sub> /p6mm 128.9 (2.2) I; I 125.2 (2.17) Col <sub>h</sub> /p6mm 39.5 (0.7) Cr				
PBSAN-9	Cr 51.9 (2.4) Col <sub>h</sub> /p6mm 133.6 (2.3) I; I 128.8 (2.17) Col <sub>h</sub> /p6mm <sup>b</sup>				
PBSAN-10	Cr 49.1 (2.4) Col <sub>h</sub> /p6mm 133.3 (2.2) I; I 130.18 (2.18) Col <sub>h</sub> /p6mm 61.8 (0.3) Cr				
PBSAN-11	Cr 112.3 (4.4) Col <sub>h</sub> /p6mm 119.5 (2) l; l 115.1 (1.9) Col <sub>h</sub> /p6mm 62.3 (4.5) Cr				
PBSAN-12	Cr 51.6 (8.9) Col <sub>h</sub> /p6mm 130.2 (1.8) I; I 125.4 (1.6) Col <sub>h</sub> /p6mm 53.1 (1.0) Cr				
PBSAN-14	Cr 82.9 (9.7) Col <sub>h</sub> /p6mm 127.8 (2.4) I; I 125.6 (2.2) Col <sub>h</sub> /p6mm 23.5 (19.2) Cr				
PBSAN-16	Cr 51.6 (62.0) Col <sub>h</sub> /p6mm 120.2 (1.0) l; l 117.5 (0.9) Col <sub>h</sub> /p6mm 24.4 (3.6) Cr				

<sup>a</sup> Transition temperatures determined by both polarizing optical microscope (POM) and peak values of the DSC thermograms during the first heating/cooling cycles at 5 °C /min rate. <sup>b</sup> The mesophase freezes at about 65 °C which remains unchanged upto - 60 °C (limitation of the instrument).

**PBSAN-11**, **PBSAN-12** and **PBSAN-14** display an identical Col phase regardless of variations in their terminal chain length or the measurement temperatures. The high-angle area (for  $2\theta > ca$  12-15°) of all the diffractograms of the Col phase is characterized by the halo scattering corresponding to spacing (*d*) in the range of 4.3–4.56 Å, which stems due to the slow mobility of the molten *n*-alkoxy tails located on either side of the central five-ring aromatic rigid core. The Col phase of phasmidic LCs may as well display a relatively sharp scattering in the high-angle region (at Bragg angles  $2\theta \sim 25$  deg) due to an intermolecular co-facial  $\pi$ - $\pi$  interaction between the constituent mesogenic cores of a column. The lack of such an intracolumnar reflection, precisely the signature due to core-core separation, in the XRD profiles implies the like-lihood of disordered arrangement of the hexacatenar molecules within the columnar structure of samples under discussion. The low angle region ( $0 < 2\theta < 5^{\circ}$ ) of all the diffraction scans comprises a strong reflection along with three weak peaks (Fig. 4a; Table 2).

It is known that all interplanar spacing distances, and thus, the reflection peaks seen in the diffractograms will be in archetypal ratio values with reference to the first indexed peak. Thus, the spacings of these reflections were found to be in the ratio of  $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$ , which could be indexed to (100), (110), (200), and (210) reflections of a guasi 2D hexagonal lattice. Thus, the investigated compounds show a columnar phase featuring hexagonal 2D lattice. It may be recalled here that the Col<sub>b</sub> phase formed by phasmidic LCs has the same symmetry as that of the discotic LCs. As is generally known, the indexing of a Col<sub>b</sub> phase, belonging to the  $D_{6b}$  point group symmetry, is comparatively straightforward because of the high symmetry of the p6mm plane group, which is equivalent to the p6/mmm space group. Accordingly, the Col<sub>b</sub> phase exhibited by the present PBSAN series of compounds can be assigned with p6mm symmetry. The lattice parameter (a) determined for the Col<sub>h</sub> phase at the chosen temperatures of the mesogens has been collected in Table 2. As envisaged, the value of 'a' increases with the elongation of long terminal tails, meaning yet again



**Fig. 2.** POM images of the thin-films of Col<sub>h</sub> phase realized by cooling the representative samples from their isotropic phase contained between two untreated glass substrates: (a) The *pseudo* focal-conic fan-like (planar) texture of **PBSAN-10** (at 90 °C), (b) the *pseudo* isotropic (homeotropic) pattern accompanied by linear birefringent defects seen for **PBSAN-11** at 110 °C and (c) the spherulitic /fan-shaped birefringent pattern along with the homeotropic texture shown by **PBSAN-14** at 105 °C.



Fig. 3. DSC traces recorded for the two successive heating (h1,h2)-cooling (c1, c2) cycles at a rate of 5 °C for (a) PBSAN-9 and (b) PBSAN-14. Note that the peak positions of all the traces match implying that the PBSAN LCs are heat and moisture resistant. Notice that compound PBSAN-14 crystallizes during the second heating cycle.



Fig. 4. 1D intensity vs  $2\theta$  profiles obtained for the Col<sub>h</sub> /p6mm phase of compounds **PBSAN-11**at 90 °C & 110 °C (a), and **PBSAN-14** at 80 °C & 105 °C (b). Front view of a slice (disk-like columnar core) resulting from the spontaneous self-assembly of a pair of phasmidic mesogens in a side-by-side fashion via  $\pi$ - $\pi$  interaction (c). Schematic diagram of the Col<sub>h</sub>/p6mm phase where the directionally correlated tilting of the slices within the columns is non-existent (d).

that the fundamental Col structure of all the compounds studied here is indistinguishable.

However, the Col<sub>b</sub> phase of hexacatenars differs from that of the conventional discotic LCs in comparison to the molecular arrangements within the columns. About two to several phasmidic molecules, driven by the secondary forces (viz., H-bonding,  $\pi$ - $\pi$  interaction, van der Waals correlation, etc.), self-assemble in a side-by-side manner to vield a slice (molecular disk/core or disk-like stratum), and the slices thus generated stack on top of one another to yield indefinitely long columns constituting a hexagonal 2D lattice. Precisely, the well-extended columns are shaped or filled with slices comprising a minimum of two phasmidic mesogens (Fig. 4c). However, the slices may have either upright or tilted orientation with respect to the columnar axis in the LC phase. In order to figure out these aspects, the XRD results of the Col<sub>h</sub> phase along along with the molecular mass (M) values of the materials were used. As can be seen in Table 2, the intercolumnar distance, the lattice parameter (a) derived, is notably smaller than the diameter (molecular dimension) of the fully stretched all-trans conformation of the hexacatenars. With the literature survey results on this subject in hand, this feature can be obviously attributed to the tilting of slices with respect to the cross section of each column. The tilt angle ( $\theta$ ) of the 2D slice with respect to the normal to the columnar axis (i.e. along the longitudinal slice direction) was estimated using an expression  $\theta = 90$ -cos<sup>-1</sup>(*a*/*L*) where *a* and *L* respectively being the lattice parameter and length of the mesogens in their most extended geometrical form with an all-trans conformation of the alkoxy chains. Accordingly, the measured tilt angles of the stacked molecules in the Col phase are: 37° for PBSAN-11 and 42° for both PBSAN-12 and PBSAN-14.

The average number of molecules (*Z*) constituting a slice of the columns with a height of  $h = \sim 4.5$  Å, which is the broad diffuse maximum

in the wide-angle area of XRD profile, was calculated from the experimental value of the unit cell parameter (a) and assuming a density of  $\rho = 1 \text{ g cm}^{-3}$ . According to the standard expression  $Z = (\sqrt{3} a^2 h N_A)$  $\rho$ )/2 $M_{w}$ , where  $M_{W}$  is the molecular weight and  $N_A$  is Avogadro's number, about 2.1 to 2.7 phasmidic mesogens constitute each slice of the columns. That is, on an average, 2 to 3 molecules arranged in a side-by-side manner via  $\pi$ - $\pi$  interaction yield a disk-like columnar core (slice) where the self-assembled five-ring aromatic cores act as central rigid structure (hard region) and the peripheral tails not only fill the space but also serve as the fluid (soft) region of the disk (Fig. 4c). Thus, the attractive  $\pi$ - $\pi$  interactions coupled with nanophase segregation among the incompatible rigid and flexible domains of the molecules drive the formation of hexagonal columnar structure (Fig. 4d). It is important to discuss the correlation between the columnar structure and the optical textures observed under the POM. As mentioned above, the pairs of molecules (slices) tilt within the columns, and the average tilt angle is expected to be nearly the same in different columns. This directionally correlated tilting obviously reduces the symmetry of the macroscopic structure, meaning that the mesophase should be optically biaxial and thus, the occurrence of homeotropic texture is ruled out. However, on the contrary, the Col<sub>h</sub> phase formed by the PBSANs show homeotropic patterns predominantly, implying that the directionally correlated tilting among the columns does not exist. That is, the tilt direction of the slices within the columns is not correlated (Fig. 4c), and thus, the homeotropic texture is seen.

# 2.3. Photophysical studies

ESIPT is an exceptional four-level photochemical (E-E\*-K\*-K) process wherein the photoexcited molecules relax their energy via

The results of (*hkl*) indexation of XRD profiles recorded at the specified temperature (T) of the columnar hexagonal phase of representative phasmidic LCs viz., **PBSAN-11**, **PBSAN-12** and **PBSAN-14**.

Compound (L/Å)	Phase (T/°C)	d <sub>obs</sub> (Å)	d <sub>cal</sub> (Å)	Miller indices hkl	a: Lattice parameter (Å) S: Lattice area (Å <sup>2</sup> ) V: Molecular volume (Å <sup>3</sup> ) Z: Number of molecules per column slice
PBSAN-11 (55.1)	Colh	33.21	33.20	100	a = 38.34
	90	19.17	19.17	110	S = 1273.01
		16.57	16.60	200	V = 5690.39
		12.55	11.67	210	Z = 2.17
		4.47			
	Colh	33.31	33.30	100	a = 38.46
	110	19.25	19.23	110	S = 1281
		16.62	16.65	200	V = 5713.26
		12.70	11.70	210	Z = 2.18
		4.46			
PBSAN-12 (56.6)	Col <sub>b</sub>	37.94	37.93	100	a = 43.80
	80	21.87	21.90	110	S = 1661.41
		19.02	18.96	200	V = 7210.55
		14.46	14.33	210	Z = 2.53
		4.34			
	Col <sub>b</sub>	37.93	37.92	100	a = 43.79
	100	22.21	21.89	110	S = 1660.6
		18.92	18.96	200	V = 7290.21
		14.42	14.33	210	Z = 2.51
		4.39			
PBSAN-14 (57.8)	Col <sub>h</sub>	41.03	41.02	100	a = 47.37
	80	24.79	23.68	110	S = 1943.20
		20.56	20.51	200	V = 8647.63
		15.60	15.52	210	Z = 2.70
		4.45			
	Col <sub>h</sub>	41.10	41.09	100	a = 47.45
	105	24.20	23.72	110	S = 1949.85
		20.61	20.54	200	V = 8891.35
		15.61	15.53	210	Z = 2.73
		4 56			

L = Length of the polycatenar mesogen estimated in its all-*trans* conformation from Chem 3D Pro 8.0 (Molecular model software from Cambridge Soft).  $d_{obs}$ : Spacing observed;  $d_{cal}$ : spacing calculated (deduced from the lattice parameter 'a' for the Col<sub>h</sub> phase).

tautomerization from Enol (E)-form to Keto (K)-form essentially involving intramolecular proton-transfer (PT) process. [73-82] As illustrated in Fig. 5, PBSAN molecules, being ESIPT fluorophores, stay in thermodynamically favored enol-imine (OH) tautomeric form at the ground (E, S<sub>0</sub>) state due to the presence of H-bridged, the quasi six-membered ring formed by the intramolecular H-bonding between the H-atom and N-atom of the hydroxy and imine groups respectively (Fig. 5). After light absorption, the singlet excited (S<sub>1</sub>, E<sup>\*</sup>,) state of the enolform, due to photoexcitation, gets populated but without the relaxation of the geometry, which is in accordance with the Franck-Condon principle. The excited enolic state (E<sup>\*</sup>), which may experience a radioactive decay (emission) and revert to the original enolic form (E), necessarily undergoes ESIPT process much ahead of fluorescence, on a time scale ranging from femtoseconds (fs) to picoseconds (ps), yielding the excited ketone species (K\*, S1'). This means that ESIPT invariably occurs due to the keto tautomer. The excited ketone (K\*) state decays to attain ketone ground (K, S<sub>0</sub><sup>\*</sup>) state with the emission of light at lower energy than the E\* form; the large Stokes shift in fluorescence occurs due to the significant reorganization of the geometry. Subsequently, a reverse PT takes place to produce the fundamental enol-form. Thus, PBSAN mesogens should display dual emission - the first (normal) one at lower wavelengths is due to enol-emission and second one at higher wavelengths with large Stokes shift resulting from the keto-tautomer formed after PT (Fig. 5).

Thus, to illustrate the aforesaid novel four-level photochemical phenomenon of the **PBSANs** realized in this study, photophysical measurements were carried out. UV–Vis electronic absorption and emission spectra of the solid samples, in the form of drop-casted thin-films, and dilute solutions of the compounds in dichloromethane (DCM) ( $c = 1 \times 10^{-4} \text{ mol L}^{-1}$ ) using quartz cells were recorded at

room temperature. The temperature-dependent photoluminescence spectra for the Col<sub>h</sub>/p6mm phase were recorded for two representative samples; in this mode, the emission spectra were also recorded in the isotropic liquid state and solid/frozen Col phase of the samples. Given the fact that all the members of the series vary structurally only with respect to the length of terminal tails, they are expected to display identical photophysical properties. Thus, all the hexacatenars exhibited analogous UV-Vis and fluorescence spectra. As shown in Fig. 6a, the DCM solutions of the mesogens exhibit two distinct absorption maxima viz., a strong band at ~360 nm and a weak peak at ~270 nm (Table 3) possibly arising due to the  $\pi$ - $\pi^*$  and n- $\pi^*$  transitions respectively. Given the fact that the hexacatenars are characterized by the strong intramolecular H-bonding, the aforesaid UV-Vis bands arising due to aggregation of the mesogens can be ruled out. As shown in Table 3, the molar extinction coefficients  $(\varepsilon)$  determined for the higher wavelength band were found to be in the range of  $1.8 \times 10^4$  to  $5.7 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup> (Table 3).

Seemingly, the absorption bands fall in the UV region due to high absorption coefficients implying that these materials readily absorb photons. The corresponding emission spectra recorded for the excitation wavelength of 365 nm showed an intense peak at ~610 nm with a broad shoulder at ~660 nm; in addition, a weak absorbance band at ~430 nm exists in the spectra of some members of the series (Fig. 6b). It may be mentioned here that the colour of these solutions, appearing yellow under daylight (Fig. 6b - left-inset and Fig. S23a), turns intense orange when exposed to 365 nm light (Fig. 6b- right-inset and Fig. S23b). The strong band located at around 610 nm can be attributed to ESIPT emission, whereas the less intense, blue-shifted band occurring at ~430 nm can be ascribed to the normal emission. It is immediately apparent from the data collected in Table 3 that the Stokes shift is in the



Fig. 5. Schematic representation of the ESIPT (four-level photochemical) process proposed for the PBSAN materials studied in this work.

range of 250–256 nm; this is important given the fact that the large Stokes shift prevents the self-absorption of the dyes or the inner filter effect. Such a large Stokes shift observed here for the ESIPT chromophores can be attributed not only to the geometry relaxation but also to the drastic change in geometry of the keto-form when compared to that of the enol-tautomer. It may be worth mentioning here that the fluorescence peak position and/or intensity appears to depend on the polarity of the solvent used, which is shown in Fig.S24.

The dependence of fluorescence intensity on the concentration was probed for a representative material. The emission spectra recorded, for the excitation wavelength of 365 nm light, at the different concentrations of **PBSAN-12** in DCM revealed that the fluorescence intensity indeed increases with the increase in the concentration of the solute (Fig. S25a), as expected. Fig. S25b shows that the intensity of ESIPT (keto) fluorescence intensity when compared to that of the normal (enol) one, increases progressively with an increase in the



**Fig. 6.** UV–Vis absorption (a) and photoluminescence spectra (b) of **PBSAN**-*n* series of mesogens at  $c = 1 \times 10^{-4}$  mol L<sup>-1</sup> in DCM. Insets of (b) are the photographs of the solution of **PBSAN-8** in DCM under daylight (left) and that exposed to UV light at 365 nm (right).

Photophysical data derived from the UV-Vis and photoluminescence spectra of PBSAN-n series of LCs recorded for their dilute DCM solutions and the solid (thin-film) states.

LCs	Solution		Stoke	Extinction coefficient	Solid (Thin-film)	Solid (Thin-film) <sup>d</sup>	
	Absorption <sup>a</sup> $[\lambda_{abs}, (nm)]$	Emission <sup>a,b</sup> [λ <sub>em</sub> , (nm)]	shift <sup>c</sup>	hift <sup>c</sup> (L/mol.cm)	Absorption <sup>d</sup> $[\lambda_{abs}, (nm)]$	Emission <sup>b</sup> [λ <sub>em</sub> , (nm)]	shift <sup>c</sup>
PBSAN-5	280,363	614	251	$5.08 \times 10^{4}$	275, 354	629	275
PBSAN-6	265, 360	614	254	$2.43 \times 10^{4}$	273, 353	629	276
PBSAN-7	286, 359	615	256	$2.95 \times 10^{4}$	276, 359	628	269
PBSAN-8	278, 362	614	252	$5.40 \times 10^{4}$	278, 356	629+	273
PBSAN-9	280, 364	614	250	$5.77 \times 10^{4}$	278, 360	$626^{+}$	266
PBSAN-10	281, 364	614*	250	$4.59 \times 10^{4}$	278, 355	$626^{+}$	271
PBSAN-11	279, 364	614*	250	$5.46 \times 10^{4}$	273, 353	625	272
PBSAN-12	286, 361	615*	254	$3.14  imes 10^4$	278, 360	$624^{+}$	264
PBSAN-14	267, 360	615*	255	$1.84  imes 10^4$	277, 357	$625^{+}$	268
PBSAN-16	279, 364	614*	250	$3.83  imes 10^4$	278, 361	629	268

\*A less intense, broad band exists at 430 nm (see Fig. 6b).

<sup>+</sup>A less intense but broad peak occurs at 435 nm (see Fig. 7b).

<sup>a</sup>Absorption and fluorescence spectra were obtained for the DCM solution of the samples. <sup>b</sup> The excitation wavelength was set at 360 nm. <sup>c</sup> Stoke shift = Difference between the position of the peak maxima of the absorption band and the maximum of the fluorescence emission. <sup>d</sup> Drop-casted thin-films were made by placing dilute DCM solution of the samples on a quartz plate.

concentration of the dye. The band maximum of the emission peak as well as fluorescence (photoluminescence) quantum yield ( $\Phi_{FL}$ ) of the keto-tautomer fluorescence band, unlike that of the normal band, depend on several vital parameters, including the surrounding medium (environment). Thus, relative  $\Phi_{FL}$  of compound **PBSAN-12**, as a representative case, was measured by the comparative method where Nile red dissolved in DMSO was used as an internal standard (Fig. S26). The expression employed for the calculation of  $\Phi_{FL}$  along with the relevant details, has been given in SI. The quantum efficiency of this mesogenic dye for the longer emission was determined to be 0.12. These results are in complete agreement with the fact that emission from the ESIPT state is characterized by a large Stokes' shift that enables longer wavelength fluorescence by UV excitation and has the tendency to possess low  $\Phi_{FL}$  because of non-radiative deactivation events taking place at the keto-form excited (K\*) state. [76]

The majority of the organic fluorophores fluoresce highly in their dilute solution with high fluorescence quantum efficiencies. However, the emissive behavior in their two condensed states viz., solid-state and liquid phase is generally feeble, and even remains absent, owing to the aggregation-caused quenching (ACQ) process; this is also applicable to another condensed state, namely LC state of the mesogenic dyes. In order to circumvent the ACQ concern, a number of strategies have been explored to contain the other radiationless deactivation processes occurring at the excited state; of these, aggregation-induced emission (AIE) and aggregation-induced enhanced emission (AIEE) appear to be interesting. [76] Thus, the three condensed states viz., solid, Col LC phase, and isotropic liquid state of synthesized materials were probed for their ESIPT fluorescence competence. The solid samples drop-casted, using their DCM solutions, onto quartz substrate affording the thin-films were used to collect both UV – Visible and photoluminescence spectra. Fig. 7a and b respectively portray the absorption and emission spectra of the thin-films of mesogens. The thin-film pictures of **PBSAN-12** as seen in the daylight and after exposure to UV light (365 nm) are shown as insets in Fig. 7b. UV–Vis spectra of the films possess two distinct absorption maxima, one being weak in the range of 273–278 nm and another strong band in the range of 353–361 nm. These longer and shorter wavelength bands of the samples possibly arise due to n- $\pi^*$  and the  $\pi$ - $\pi^*$  transitions, respectively.

The photoluminescence spectra recorded for an excitation wavelength of 360 nm, the wavelength of maximum absorbance of the thin-films, are presented in Fig. 7b. Apparently, some of the thin-films possess two emission bands at ~435 nm (weak) and ~ 625 nm (strong) arising due to intramolecular proton transfer process via an excited state. The occurrence of a strong longer wavelength fluorescence band in all the films with large Stokes shift (266 to 276 nm) suggests that ESIPT process takes over the relaxation of the excited enolic (E\*) state to the original enolic form (E). The temperature-dependent photoluminescence measurements on the fluid / frozen Col LC phase along with the isotropic liquid state were performed for the two representative materials namely, **PBSAN-9** and **PBSAN-12**; their respective



Fig. 7. The electronic absorption and photoluminescent spectra (a and b) of the drop-casted thin-films of the PBSAN-*n* series of compounds. The thin-film pictures of PBSAN-12 as seen before, inset of (b)-top, and after the illumination with UV light (365 nm), inset of (b)-bottom.

phase sequences and transition temperatures (in parenthesis,  $^{\circ}$ C) noted during the cooling cycle are: I (128.8) Col<sub>h</sub> – freezes at about 65, and I (125.4) Col<sub>h</sub> (53) Cr. The samples held between quartz plates in minute quantities were slowly heated to 150 °C (well above their isotropization temperature) using a programmable hot stage where the top quartz substrate of each cell was pressed hard to spread the sample evenly. Fig. 8a and c respectively depict the fluorescence spectra recorded at varying temperatures for the samples (excited at 360 nm) **PBSAN-9** and **PBSAN-12** at 10 °C interval while cooling them from 150 °C to 40 °C.

The spectral signatures of both samples in their liquid state (in the temperature range of 130 to 150 °C) and fluid/frozen Col<sub>h</sub> phase (50 to 120 °C), were found to be virtually similar, except for peak intensities, displaying dual-fluorescence emission; indeed, the analogous spectral pattern was seen for the solid-state (40 and 50 °C) of **PBSAN-12** (Table S1). The weak emission appearing around 465 nm could be ascribed

to enol-form ( $E^{*}-E$ ), whereas the emission band at a longer wavelength, existing around 630 nm, can be convincingly assigned to keto-tautomer ( $K^{*}-K$ ).

As mentioned earlier, whereas the pattern of the temperature-dependent fluorescence spectra of the samples remains indistinguishable, their ESIPT photoluminescence (K\*-K) intensity increases gradually with the decrease in temperature; this also true for the intensity of normal emission. However, as shown in Fig. 8b and d, the magnitude of ESIPT fluorescence intensity of the Col phase belonging to both the mesogens, when compared to that of the normal (E\*-E) fluorescence emission, depends remarkably on the temperature that can be attributed to the breaking of larger aggregates or thermally activated non-radiative transitions [65,83–87]. Interestingly, the emission maxima of the ESIPT fluorescence spectra, recorded while progressive cooling of the Col phase of the compounds **PBSAN-9** and **PBSAN-12**,



**Fig. 8.** Fluorescence spectra recorded as a function of temperature in the Col<sub>h</sub> phase which includes isotropic liquid and solid states of compounds **PBSAN-9** (a) and **PBSAN-12** (c); notice here that the spectral signatures are identical in all the three condensed states, i.e. liquid state, fluid/frozen Col<sub>h</sub> LC phase and solid state. The temperature-dependence of the magnitude of ESIPT fluorescence emission intensity and the normal (E\*-E) fluorescence intensity of **PBSAN-9** (b) and **PBSAN-12** (d). The bathocromic shift of ESIPT fluorescence emission maxima observed while cooling **PBSAN-9** (e) and **PBSAN-12** (f) from 150 °C to 40 °C implying J-aggregation.

seem to shift marginally, by and large, towards red (longer wavelength) end of the spectrum (Fig. 8e and f).

This demonstration of narrow bathocromic shift of the emission maxima upon decreasing the temperature without photoluminescence quenching of the Col phase (formed by the self-assembly of mesogens in the manner mentioned above) imply the formation of so-called Scheibe or [-aggregates [88–90] where the  $\pi$ - $\pi$  stacked aromatic cores within the columns, oriented in a head-to-tail manner, tilt with respect to the column axis of the column (Fig. 4c); this behavior completely agrees with the Col LCs reported earlier. [65,91,92] The occurrence of J-aggregates can be figured out by determining the tilted angle between the molecular plane and the aggregation (packing) direction. As per the exciton-coupling theory [93,94], in the J-aggregates, wherein the dipoles maintain a head-to-tail orientation of the constituent fluorophores, and the tilted angle should be less than 54.7 degrees. The results of X-ray diffraction analysis revealed that the tilted stacking angle measured for PBSAN-12 is less than the aforesaid theoretical value viz. 42 degrees. This means that the phasmidic fluorophores spontaneously self-assemble, through the strong  $\pi$ - $\pi$  interactions (but not through intermolecular H-bonding), into indefinitely long J-aggregates (columns), which in turn arrange on a 2D hexagonal lattice (Fig. 4d).

To corroborate the aforementioned photophysical results, the structural and energy parameters viz., electron distribution and band-gaps (energy levels) of the HOMO (highest occupied molecular orbital) and LUMO for the enol-imine (E)/(OH) and keto-enamine (K)/(NH) states of a representative material **PBSAN-12**, were obtained by the Hartree Fock (HF) and Density-functional theory (DFT)-based calculations. The HF calculations were performed using RHF single point energy functional and DFT calculations using B3LYP functional in conjunction with the def2-TZVP basis set in ORCA 4.01 software [95]. The optimized structures along with the HOMO and LUMO electron distribution and the energy values/levels obtained from these (DFT and HF) studies have been depicted in Fig. 9 (also see Figs. S27 and S28), and the relevant data are collected in Table 4. The optimized structures of both enol and keto states (Fig. S28), the former being thermodynamically stable than the latter, reveal the coplanar conformation between hydroxyl and imine/keto and enamine groups that can be ascribed to the presence of strong intramolecular H-bonding, which accounts for the stability of different tautomeric forms of mesogens. That is, the intramolecularly H-bonded cis-enol and cis-keto forms exist in the optimized structures.

Apparently, the band gaps and electron densities are different for enol and keto forms. According to the data presented in Table 4 (Fig. 9), the HOMO energy level of keto-enamine form is higher than that of the enol state. In the enol-imine (OH) form, the HOMO orbitals are evenly localized on the central three benzene-rings whereas the LUMO orbitals are delocalized mostly on the central benzene-ring where both hydroxyl and imine groups are located; it is especially



Fig. 9. Theoretical parameters of ESIPT active mesogen PBSAN-12 (a representative case) derived from the DFT calculations: The optimized conformation structures, electron density distributions in the HOMO and LUMO states of enol-imine (OH)/(E) and keto-enamine (NH)/(K) forms, and HOMO-LUMO energy levels (band-gaps).

Theoretically calculated HOMO–LUMO energy levels and band gap values derived from both theory and experimental measurements.

Parameters of <b>PBSAN-12</b>	Enol-Imine (OH) form		Keto-Enamine (NH) state	
	HF	DFT	HF	DFT
HOMO (eV)	-7.8	-5.6	-6.9	-4.4
LUMO (eV)	1.0	-2.3	0.9	-2.4
$\Delta E (eV)$	6.8	3.3	6.0	2.0
$\Delta E$ (eV) (Experimental)	3.3 (~ 376 nm)		2.0 (~ 621	)

visible that in the LUMO state the electronic density at the nitrogen atoms relatively more and thus they act as proton acceptor implying that, the proton transfer is favored after the absorption of photons. It is clear from the Fig. 9 that, in the keto-state, the HOMO is concentrated on three benzene-rings and the LUMO is localized on the keto and enamine groups. The HOMO-LUMO energy gaps derived from the DFT calculations for enol and keto states are 3.3 eV (376 nm) and 2.0 eV (621 nm), respectively; the corresponding experimentally measured values were found to be 2.8 eV (430 nm) and 2.0 eV (621 nm). Seemingly, the theoretical and experimental HOMO-LUMO band gap values of the keto-form are in good agreement with each other. Overall, this theoretical study undertaken here clearly substantiates the experimentally observed photo-excitation induced ESIPT occurring in the phasmidic LCs synthesized.

# 2.4. Electrochemical properties

The cyclic voltammetry (CV) technique was employed to study the reduction and oxidation characteristics of the ESIPT active mesogens synthesized. As representative cases, PBSAN-9, PBSAN-11, and PBSAN-16 were examined for their redox behavior by using a conventional three-electrode cell comprising a set of working electrode, counter electrode, and reference electrode. While the reference electrode determines the applied potential, the current flows between the counter and working electrodes. Precisely, Ag/AgCl (reference electrode), platinum rod (working electrode), and platinum wire (counter electrode) were employed. TBAPF6 (tetrabutylammonium hexafluorophosphate, 0.1 M) in acetonitrile (HPLC grade) was used as a supporting electrolyte. The room temperature measurements were conducted at a scanning rate of 0.5 mVs<sup>-1</sup>. Ferrocene /ferrocenium ion (Fc/Fc+) couple was employed as the internal reference, and all the potentials were calibrated with the same system; here, it assumed that the energy level of the Fc/Fc + pair is 4.8 eV below the vacuum level. The samples used for analysis were the same as those for UV-Vis experiments. As depicted in Fig. S29, all the mesogens functional groups such as hydroxyl and imine segments in their molecular structure. The energy levels of the HOMO and LUMO were determined using the formulas  $E_{HOMO} = -(4.8 + E_{ox,onset})$  eV and  $E_{LUMO} =$  $-(4.8 + E_{red,onset})$  eV. The electrochemical band-gap ( $\Delta E_{g,CV}$ ) between the frontier orbitals was determined using the expression  $\Delta E_{g.CV} =$  $E_{HOMO}$  -  $E_{LUMO}$  eV. The optical band gap  $(\Delta E_{g,opt})$  values were figured out from the longest wavelength absorption onset of the absorption spectra of mesogens by using the expression  $E = 1240 / \lambda_{onset}$ . The electrochemical band gap values of these mesogens determined using their voltammograms and absorption spectra are in the range of 1.17-1.22 eV and 2.40-2.54 eV respectively (Table 5). The comparison reveals that the electrochemical band gaps are lesser than those derived from the optical method and such discrepancy can be ascribed to several factors such as the electrode characteristics (size, surface, heterogeneity), media (the status of electrolyte -oxygen content), pre-adsorbed gases, molecular adsorption/desorption, double layer charging/discharging, 2D surface diffusion etc. However, it appears that the electrochemical band gaps of the compounds (ca 2.5 eV) are relatively closer to the Table 5 Electroche

lectrochemical	properties	a of repi	resentativ	e compou	ınds.	
	1.					

Mesogens	E <sup>b</sup> oxd	E <sub>HOMO</sub> (eV)	E <sup>b</sup> red	E <sub>LUMO</sub> (eV)	$\Delta E_{g,CV}^{c}(eV)$	E <sup>d</sup> <sub>g.opt</sub> (eV)
PBSAN -9	1.04	-5.84	-0.18	-4.62	1.22	2.40
PBSAN - 11	0.96	-5.76	-0.20	-4.59	1.17	2.54
PBSAN - 16	1.00	-5.80	-0.17	-4.63	1.17	2.53

<sup>a</sup> Experimental conditions: Room temperature measurements with a scanning rate of 0.5 mVs<sup>-1</sup>; Ag/AgCl reference electrode, Pt-rod working electrode, Pt-wire counter electrode and TBAPF6 (0.1 M) in HPLC grade acetonitrile as a supporting electrolyte.

<sup>P</sup> Estimated from the onset oxidation and reduction potential (vs Ag/Ag<sup>+</sup>) plus 4.8.

<sup>c</sup> Electrochemical band gaps were calculated from E<sub>HOMO</sub> and E<sub>LUMO</sub>.

<sup>d</sup> Optical band-gaps were determined from the red edge of the longest wavelength from the UV–Vis absorption of mesogens.

bandgap value viz.,3.3 eV derived from theoretical calculations for their homolog **PBSAN-11.** Therefore, one can assume that these mesogens may have bandgap of about 3.0 eV and thus, they can be regarded as wide-bandgap semiconducting columnar LC materials having the electronic characteristics falling between those of conventional semiconductors and insulators. This hypothesis is also supported by the fact that the electronic absorption and ESIPT phenomenon of these novel mesogens respectively take place in the near-ultraviolet and visible spectral ranges.

As described earlier, in the ESIPT phenomenon, the photoexcited mesogens relax their energy by converting themselves from enol-state to keto-form wherein intramolecular PT occurs. Thus, the presence of hydroxyl (-OH) group enabling intramolecular PT is essential for the ESIPT process to happen. This means that the ESIPT activity is basically governed by the electronic environment of both imine (proton acceptor) and oxygen atom of the hydroxyl group (proton donor) of the cis-enol tautomer. Needless to say, by varying the electron density at the nitrogen (acceptor) atom and/or oxygen (donor) atom, the proton transfer process leading to dual emission property of ESIPT active molecules can be modulated. One of the well-known methods of accomplishing this task is to treat such fluorophores with metals forming cations (metal-ions). From another standpoint, one can say that with the help of such binding studies, the occurrence of ESIPT process in functional materials can be evidenced with great ease. Hence, the phasmidic LCs, having two binding (chelating) sites, each consisting of a hydroxyl group and an imine unit, were screened for their binding abilities in solutions with different metal ions such as Cr<sup>6+</sup>, Mn<sup>2+</sup>, Hg<sup>2+</sup>, Au<sup>3+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup> and Fe<sup>3+</sup>. The binding (chelating) ability of a representative ligand PBSAN-16 for the aforesaid metal ions was tested by monitoring changes in light emission properties. The titrated solutions, obtained after the drop-wise addition of metal salt (CrO<sub>3</sub>, MnCl<sub>2</sub>, Hg(OAc)<sub>2</sub>, HAuCl<sub>4</sub>, Zn(OAc)<sub>2</sub>, Cu(OAc)<sub>2</sub>, NiCl<sub>2</sub>, FeCl<sub>3</sub>) solutions (50 µL) in DMF (c = 0.5 M) to the 10 mL of **PBSAN-16** in DCM (c =  $10^{-4}$  M), were subjected to their photoluminescence behavior. The photographs obtained for the probe PBSAN-16 in DCM and those of the titrated solutions under 365 nm light are shown in Fig. 10a and Fig. 10b, respectively. The emission spectra recorded for these titrated solutions, excited at 365 nm, are shown in Fig. 11.



Fig. 10. Photographs captured under a UV lamp (365 nm) for the mesogen PBSAN-16 in DCM before (a) and after treating with the various metal salts in DMF (b).



**Fig. 11.** (a) Photoluminescence spectra recorded at room temperature for the solutions formed by treating the probe **PBSAN-16** in DCM with different metal salts in DMF; (b) fluorescence spectra of ligand **PBSAN-16** in DCM (red-trace) and after treating with Zn<sup>2+</sup> ions (green-trace) (Excitation wavelength is 360 nm).

The presence of Cr<sup>6+</sup> and Fe<sup>3+</sup> ions alters drastically the photoluminescence profile of the ligand PBSAN-16 where the bands due to dual fluorescence pertaining to the normal and ESIPT emissions vanish completely (Fig. 11a) that can be ascribed to the collisional quenching coupled with the formation of coordination complexes. The complex formation especially disrupts ESIPT activity of the probe molecules. The addition of  $Cu^{2+}$  and  $Ni^{2+}$  also perturbs the emission property of the ligands to the extent that the ESIPT band (~ 600 nm) remains absent that can be attributed yet again to the formation of complexes; however, the existence of three emission bands at ca 410, 430 and 460 nm, suggests that the coordination compounds generated are photoluminescent. More or less, no changes in the emission spectra were noticed when  $Mn^{2+}$ ,  $Hg^{2+}$  and  $Au^{3+}$  ions were treated with the ligand, implying that these metal ions do not chemically interact with probe molecules. Interestingly, as shown in Fig. 11b, the interaction of Zn<sup>2+</sup> ions with **PBSAN-16** molecules not only augments the fluorescence emission intensity but also shifts the ESIPT peak towards a shorter wavelength (blue shift). In essence, these experiments clearly substantiate the fact that the phasmidic molecules studied here not only are ESIPT active but also can serve as chemosensors.

# 3. Conclusion

In this article, we have presented the synthesis, structural characterization, mesomorphism, photophysical behavior, redox activity, metal ion sensing ability and solvatochromism of ten new, ESIPT active, phasmidic bis(N-salicylideneaniline) LCs belonging to a homologous series. They have been readily synthesized with notable yields by the acidcatalyzed condensation of two moles of lipophilic (half-disk shaped) amines with one mole of 2,3-dihydroxyterephthalaldehyde. These ohydroxy Schiff bases, being resistant to heat and moisture, which can be attributed due to the presence of hydrogen (H)-bridged quasi sixmembered rings, display columnar LC phase. The optical textural patterns combined with XRD data analysis confirm the presence of Col<sub>h</sub> having p6mm symmetry. XRD results imply that the slices (disk-like columnar core), formed by the self-assembly of two molecules in a sideto-side fashion, tilt with respect to the columnar axis and tilt direction among the columns is not correlated; the profiles also show that the core-core (slice-to-slice) interactions are too weak. Photophysical measurements clearly revealed the intrinsic ESIPT phenomenon not only in their dilute solutions but also in their solid, liquid crystal (Col) phase and isotropic liquid state. In the Col<sub>h</sub> phase, the magnitude of ESIPT fluorescence emission intensity display temperature-dependence; the emission maxima shifts to longer wavelengths upon decreasing the temperature confirming the J-type aggregation in the mesophase. Electron distribution in the optimized structures and band-gaps of the HOMO and LUMO for the enol and keto states determined by HF and DFT-based calculations support the photophysical experimental observations. The evaluation of metal ions chelating property reveals that a mesogen (as a representative case) selectively binds to certain metal ions to form metal complexes; notably, the complex formation of mesogen with  $Zn^{2+}$  ions not only enhances the emission intensity but also shifts the peak towards shorter wavelength. The electrochemical band gap values determined from the CV experiments appear to match with those derived from the theoretical calculations closely. In essence, these phasmidic columnar LCs exhibiting ESIPT phenomenon and other physicochemical properties may serve as functional materials for various technological applications.

# 4. Experimental

# 4.1. IGeneral remarks

# 4.1.1. General information (materials and methods)

Gallicacid, n-alkylbromides, 4-nitrophenol and 1,2-dimethoxvbenzene procured from Sigma-Aldrich Company were utilized as received. Organic solvents employed for various general purposes were distilled prior to use. Silica gel thin layer chromatography (TLC) was used to monitor the progress of the organic reactions and also assess the purity of the compounds synthesized, especially the intermediates. In particular, TLC plates consisting of a thin layer of silica gel (Merck, Kieselgel60, F254) on an aluminium foil backing were employed. The column chromatography was performed using glass columns packed, by the wet method, with either neutral alumina or silica gel (60-120/ 100-200 mesh) as the solid support. UV-Vis spectra of the samples were recorded using Perkin-Elmer's Lambda 750, 2015 NIR spectrophotometer. FTIR spectra of the samples were obtained from Perkin-Elmer Spectrum 1000 FT-IR spectrometer, and the typical unit used in the spectra is wave numbers (which is  $cm^{-1}$ ). Fluorescence emission (photoluminescence) spectra of all the ESIPT active molecules synthesized were collected, in their solid, solution amd LC phases, using a spectrofluorometer Flurolog-3, Horiba Jobin Yvon. Nuclear magnetic resonance (NMR) spectra were recorded with the help of a Bruker AMX-400 spectrometer operating at 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C. The <sup>1</sup>H NMR chemical shifts ( $\delta$ ) are presented in parts per million (ppm) relative to tetramethylsilane (TMS) peak ( $\delta$  0.0). The spectra were obtained at room temperature from solutions of the samples dissolved in deuterated chloroform (CDCl<sub>3</sub>) with residual solvent serving as internal standard (7.26 ppm for <sup>1</sup>H and 77.16 ppm for <sup>13</sup>C). The data (the nature of the proton NMR peaks) are reported as s (singlet), d (doublet), t (triplet), and m (multiplet). The coupling constants (*J* values), calculated directly from the spectra, are given in Hertz (Hz).

Integration has been determined as the relative number of atoms. An elemental analyzer, namely, Elementar Vario MICRO Select, was employed to determine the elemental compositions of the materials. DFT calculations were performed with optimized structures using B3LYP functional in conjunction with the def2-TZVP basis set in ORCA 4.01 software. The calculations were mainly used to evaluate the electronic structural properties of phasmidic mesogens in their *cis*-enol and *cis*-keto forms. The HF calculations were performed using RHF single point energy functional.

The mesogenic materials synthesized were examined for their thermal / mesomorphic properties using an Olympus BX50 (Model BX50F4) polarizing optical microscope (POM) equipped a digital camera and a hot stage, Mettler FP82HT having FP90 central processor. Differential scanning calorimeter (DSC) traces were registered at a scanning rate of 5 °C/min using Perkin-Elmer DSC 8000 equipment. The calibration of the instrument prior to use was performed using pure indium as a standard. Powder X-ray diffraction measurements were performed with the help of either Panalytical (Empyrean) or Xenocs, Genix Cu MAR345 using Cu-K $\alpha$  (1.54 Å) radiation. The samples held in Lindemann capillaries (0.5 mm diameter) and carefully flame sealed at both ends were employed.

# 4.2. General synthetic procedure for (((2,3-dihydroxy-1,4-phenylene) bis (methanylylidene)) bis(azanylylidene)) bis(4,1-phenylene) bis(3,4,5-tris (hexyloxy)benzoate)s (PBSAN-n series)

A mixture of 2,3-dihydroxyterephthalaldehyde **(7)** (0.4 mmol,1 eq.) and freshly purified 4-aminophenyl 3,4,5-tris(alkyloxy)benzoate (0.8 mmol, 2 eq.), a catalytic amount of acetic acid in ethanol (10 mL) was refluxed under an inert atmosphere for 2 h. The pale brown solid separated upon cooling the reaction mixture was collected by filtration, washed with ethanol, and dried. The crude product was purified by repeated recrystallizations in absolute ethanol (Yield: 69–75%).

**PBSAN-5:** A brown colour solid; yield: 0.125 g (70%); IR (KBr pellet):  $\nu_{max}$  in cm<sup>-1</sup> 3434, 2955, 1729, 1615, 1585, 1188, 955, 863. UV - Vis:  $\lambda_{max} = 363$  nm,  $\varepsilon = 5.08 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 13.47 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (d, 8H, *J* = 8 Hz, Ar), 7.29 (d, 4H, *J* = 4 Hz, Ar), 7.03 (s, 2H, Ar), 4.09 (m, 12H, 6 × OCH<sub>2</sub>), 1.87 (m, 54H, 18 × CH<sub>2</sub>, 6 × CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz): 165.13, 162.23, 153.10, 150.58, 150.29, 145.78, 143.20, 123.73, 122.98, 122.39, 121.45, 120.71, 108.66, 77.37, 77.12, 76.86, 73.66, 69.36, 30.09, 29.06, 28.33, 28.27, 22.63, 22.52, 14.18, 14.13. Anal. calcd for C<sub>64</sub>H<sub>84</sub>N<sub>2</sub>O<sub>12</sub>: C, 71.62; H, 7.89; N, 2.61; Found: C, 71.84; H, 8.03; N, 2.89.

**PBSAN-6:** A brown colour solid; yield: 0.100 g (72%); IR (KBr pellet): ν<sub>max</sub> in cm<sup>-1</sup> 3435, 2930, 1729, 1619, 1587, 1183, 947, 866. UV - Vis: λ<sub>max</sub> = 350 nm, ε = 2.43 × 10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 13.47 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (d, 8H, *J* = 8 Hz, Ar), 7.29 (d, 4H, *J* = 4 Hz, Ar), 7.03 (s, 2H, Ar), 4.08 (m, 12H, 6 × OCH<sub>2</sub>), 1.86 (m, 66H, 24 × CH<sub>2</sub>, 6 × CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz): 165.13, 162.23, 153.08, 150.57, 150.28, 145.78, 143.18, 123.71, 122.98, 122.38, 121.44, 120.70, 108.63, 77.34, 77.09, 76.84, 73.69, 69.36, 31.95, 30.43, 29.59, 29.38, 26.17, 22.77, 14.20. Anal. calcd forC<sub>70</sub>H<sub>96</sub>N<sub>2</sub>O<sub>12</sub>: C, 72.63; H, 8.36; N, 2.42; Found: C, 72.91; H, 8.66; N, 2.51.

**PBSAN-7:** A brown colour solid; yield: 0.105 g (74%); IR (KBr pellet):  $\nu_{max}$  in cm<sup>-1</sup> 3432, 2926, 1731, 1617, 1586, 1186, 936, 857. UV - Vis:  $\lambda_{max} = 356$  nm,  $\varepsilon = 2.95 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 13.47 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (d, 8H, *J* = 8 Hz, Ar), 7.29 (d, 4H, *J* = 4 Hz, Ar), 7.03 (s, 2H, Ar), 4.08 (m, 12H, 6 × OCH<sub>2</sub>), 1.86 (m, 66H, 30 × CH<sub>2</sub>, 6 × CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz): 165.10, 162.21, 153.08, 150.59, 150.28, 145.79, 143.19, 122.97, 122.36, 121.40, 120.66, 108.65, 77.36, 77.10, 76.82, 73.66, 69.34, 32.01, 31.87, 30.42, 29.38, 29.12, 26.09, 22.69, 14.16. Anal. calcd for C<sub>76</sub>H<sub>108</sub>N<sub>2</sub>O<sub>12</sub>: C, 73.51; H, 8.77; N, 2.26; Found: C, 73.88; H, 9.09; N, 2.47.

**PBSAN-8:** A brown colour solid; yield: 0.120 g (71%); IR (KBr pellet):  $\nu_{max}$  in cm<sup>-1</sup> 3432, 2925, 1731, 1617, 1586, 1186, 950, 859. UV - Vis:  $\lambda_{max} = 362 \text{ nm}, \epsilon = 5.40 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ; <sup>1</sup>H NMR (400 MHz,

CDCl<sub>3</sub>): 13.45 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (d, 8H, J = 8 Hz, Ar), 7.30 (d, 4H, J = 4 Hz, Ar), 7.03 (s, 2H, Ar), 4.07 (m, 12H,  $6 \times OCH_2$ ), 1.86 (m, 90H, 36 × CH<sub>2</sub>,  $6 \times CH_3$ ) <sup>13</sup>C NMR (100 MHz): 165.13, 162.23, 153.10, 150.59, 150.29, 145.79, 143.21, 123.72, 122.98, 122.38, 121.45, 120.71, 108.66, 77.36, 77.11, 76.85, 73.70, 69.37, 31.82, 31.64, 30.38, 29.34, 25.84, 25.79, 22.77, 22.71, 14.12. Anal. calcd for C<sub>82</sub>H<sub>120</sub>N<sub>2</sub>O<sub>12</sub>: C, 74.28; H, 9.12; N, 2.11; Found: C, 74.48; H, 9.54; N, 2.31.

**PBSAN-9:** A brown colour solid; yield: 0.125 g (72%); IR (KBr pellet):  $ν_{max}$  in cm<sup>-1</sup> 3442, 2921, 1734, 1618, 1585, 1186, 954, 857. UV - Vis:  $λ_{max} = 364$  nm,  $ε = 5.77 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 13.47 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (d, 8H, *J* = 8 Hz, Ar), 7.30 (d, 4H, *J* = 8 Hz, Ar), 7.03 (s, 2H, Ar), 4.09 (m, 12H, 6 × OCH<sub>2</sub>), 1.87 (m, 102H, 42 × CH<sub>2</sub>, 6 × CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz): 165.13, 162.23, 153.09, 150.59, 145.78, 143.21, 123.71, 122.98, 122.38, 121.45, 120.70, 108.66, 77.37, 77.11, 76.86, 73.70, 69.37, 31.99, 29.69, 29.50, 29.39, 26.18, 22.78, 14.21. Anal. calcd for C<sub>88</sub>H<sub>132</sub>N2O<sub>12</sub>: C, 74.96; H, 9.44; N, 1.99; Found: C, 75.27; H, 9.73; N, 2.27.

**PBSAN-10:** A brown colour solid; yield: 0.128 g (73%); IR (KBr pellet):  $\nu_{max}$  in cm<sup>-1</sup> 3432, 2924, 1730, 1618, 1586, 1186, 959, 859. UV - Vis:  $\lambda_{max} = 368$  nm,  $\varepsilon = 4.59 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 13.46 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (d, 8H, J = 8 Hz, Ar), 7.29 (d, 4H, J = 4 Hz, Ar), 7.03 (s, 2H, Ar), 4.07 (m, 12H, 6 × OCH<sub>2</sub>), 1.85 (m, 114H, 48 × CH<sub>2</sub>, 6 × CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz): 165.13, 162.23, 153.10, 150.58, 150.31, 145.80, 143.28, 123.72, 122.98, 122.38, 121.44, 120.70, 108.63, 77.11, 76.86, 73.70, 69.37, 31.99, 29.69, 29.38, 26.17, 22.77, 14.20. Anal. calcd for C<sub>94</sub>H<sub>144</sub>N2O<sub>12</sub>: C, 75.56; H, 9.71; N, 1.87; Found: C, 75.93; H, 10.02; N, 2.03.

**PBSAN-11:** A brown colour solid; yield: 0.125 g (69%); IR (KBr pellet):  $\nu_{max}$  in cm<sup>-1</sup> 3433, 2929, 1729, 1615, 1585, 1187, 961, 859. UV - Vis:  $\lambda_{max} = 364$  nm,  $\varepsilon = 5.46 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 13.47 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (t, 8H, J = 4 Hz, Ar), 7.29 (d, 4H, J = 4 Hz, Ar), 7.03 (s, 2H, Ar), 4.09 (m, 12H, 6 × OCH<sub>2</sub>), 1.86 (m, 126H, 54 × CH<sub>2</sub>, 6 × CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz): 165.13, 162.23, 153.09, 150.589150.29, 145.79, 143.21, 123.72, 122.98, 122.38, 121.45, 120.71, 108.66, 77.36, 77.11, 76.85, 73.70, 69.37, 31.82, 31.64, 30.38, 29.34, 25.84, 25.79, 22.77, 22.71, 14.18, 14.12. Anal. calcd for C<sub>100</sub>H<sub>156</sub>N<sub>2</sub>O<sub>12</sub>: C, 76.10; H, 9.96; N, 1.77; Found: C, 76.45; H, 10.34; N, 1.94.

**PBSAN-12:** A brown colour solid; yield: 0.110 g (70%); IR (KBr pellet):  $\nu_{max}$  in cm<sup>-1</sup> 3433, 2920, 1735, 1619, 1586, 1237, 1186, 948, 855. UV - Vis:  $\lambda_{max} = 359$  nm,  $\varepsilon = 3.41 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 13.47 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (t, 8H, J = 4 Hz, Ar), 7.29 (d, 4H, J = 4 Hz, Ar), 7.03 (s, 2H, Ar), 4.08 (m, 12H, 6 × OCH<sub>2</sub>), 1.87 (m, 138H, 60 × CH<sub>2</sub>, 6 × CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz): 165.13, 162.23, 153.09, 150.59, 150.29, 145.79, 143.21, 123.71, 122.98, 122.38, 121.45, 120.71, 108.66, 77.36, 77.11, 76.86, 73.70, 69.37, 32.02, 30.44, 29.80, 29.73, 29.49, 26.18, 22.79, 14.22. Anal. calcd for C<sub>106</sub>H<sub>168</sub>N<sub>2</sub>O<sub>12</sub>: C, 76.58; H, 10.19; N, 1.69; Found: C, 76.90; H, 10.54; N, 1.83.

**PBSAN-14:** A brown colour solid; yield: 0.128 g (75%); IR (KBr pellet):  $\nu_{max}$  in cm<sup>-1</sup> 3432, 2919, 1733, 1616, 1585, 1184, 949, 857. UV - Vis:  $\lambda_{max} = 360$  nm,  $\varepsilon = 1.84 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 13.47 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (t, 8H, J = 4 Hz, Ar), 7.29 (d, 4H, J = 4 Hz, Ar), 7.03 (s, 2H, Ar), 4.08 (m, 12H, 6 × OCH<sub>2</sub>), 1.85 (m, 162H, 72 × CH<sub>2</sub>, 6 × CH<sub>3</sub>) <sup>13</sup>C NMR (100 MHz): 165.13, 162.23, 153.09, 150.59, 150.29, 145.79, 143.21, 123.70, 122.99, 122.38, 121.45, 120.71, 108.66, 77.36, 77.10, 76.85, 73.71, 69.37, 32.03, 30.44, 29.85, 29.81, 29.74, 29.49, 26.18, 22.79, 14.22. Anal. calcd for C<sub>118</sub>H<sub>192</sub>N<sub>2</sub>O<sub>12</sub>: C, 77.41; H, 10.57; N, 1.53; Found: C, 77.94; H, 10.77; N, 1.93.

**PBSAN-16:** A brown colour solid; yield: 0.105 g (71%); IR (KBr pellet):  $v_{max}$  in cm<sup>-1</sup> 3435, 2919, 1731, 1618, 1587, 1187, 947, 866. UV - Vis:  $\lambda_{max} = 364$  nm,  $\varepsilon = 3.83 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 13.47 (s, 2H, OH), 8.68 (s, 2H, CHN), 7.42 (t, 8H, J = 4 Hz, Ar), 7.29 (d, 4H, J = 4 Hz, Ar), 7.03 (s, 2H, Ar), 4.08 (m, 12H,

 $6 \times OCH_2$ ), 1.85 (m, 162H, 84 × CH<sub>2</sub>,  $6 \times CH_3$ ) <sup>13</sup>C NMR (100 MHz): 165.11, 162.21, 153.10, 150.61, 150.31, 145.80, 143.28, 123.72, 122.97, 122.36, 121.42, 120.71, 108.72, 77.35, 77.09, 76.84, 73.70, 69.40, 32.02, 30.45, 29.84, 29.80 29.45, 26.18, 22.78, 14.20. Anal. calcd for C<sub>130</sub>H<sub>216</sub>N<sub>2</sub>O<sub>12</sub>: C, 78.10; H, 10.89; N, 1.40; Found: C, 78.43; H, 11.21; N, 1.67.

# **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.

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# Appendix A. Supplementary data

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