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Jia Dai, Ke-Qing Zhao, Bi-Qin Wang, Ping Hu, Benoît Heinrich, et al.. Liquid crystal ionic self-assembly and anion-selective photoluminescence in discotic azatriphenylenes. *Journal of Materials Chemistry C*, 2020, 8 (12), pp.4215-4225. 10.1039/c9tc05829j . hal-03007434

HAL Id: hal-03007434

<https://hal.science/hal-03007434>

Submitted on 17 Nov 2020

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Liquid crystal ionic self-assembly and anion-selective photoluminescence in discotic azatriphenylenes†

Jia Dai,^a Ke-Qing Zhao,^{*a} Bi-Qin Wang,^a Ping Hu,^a Benot Heinrich^b and Bertrand Donnio^{*b}

We report on the straightforward synthesis of a new series of ionic discotic liquid crystals based on positively charged azatriphenylene. In our design, the quaternized azatriphenylene core is surrounded by four to six flexible aliphatic chains and various types of anions, including small inorganic anions (i.e. Br⁻, I⁻, NO₃⁻, BF₄⁻, PF₆⁻), and organic ones such as triflate, bis(trifluoromethylsulfonyl)imide, tosylate, saccharinate, D and L camphorsulfate, alkylsulfonates, and alkylsulfates. The mesophases and thermal behaviour of the salts were characterized by polarizing optical microscopy, differential scanning calorimetry, thermal gravimetry and small-angle X-ray scattering. A classical hexagonal columnar mesophase, i.e. p6mm-Col_{hex}, was observed for most salts. Two exotic new phases were however identified for four compounds, namely a mesophase with a hexagonal lattice of p3m1 symmetry (Hex), and another mesophase with a rectangular lattice of pseudo-hexagonal geometry (i.e. a/b = 0.3) of p2mg symmetry (Rec_{phex}). The former results from the bulkiness of the triflimide anion and the arrangement of columns into a honeycomb lattice, whereas the latter is induced by the clustering of three columns, disposed according to a low-symmetry rectangular lattice. Their temperature ranges and stabilities strongly depend as expected on the anion type and the number (and length) of the alkyl side-chains (O- and N-alkyl, respectively), highlighting the delicate balance and interplay between van der Waals, electrostatic and p-p core interactions. The UV/Vis absorption and fluorescent emission spectra were measured, and a strong yellow light photoluminescence was observed depending on the anion type, whereas anion-selective luminescence was observed in thin films. The neutral azatriphenylene precursor, 6,7,10,11-tetrakis(hexyloxy)dibenzo[f,h]isoquinoline, is also an interesting luminophore, showing an absolute emission quantum yield of 75%, while the corresponding salts exhibit anion-selective emission quantum yields as high as 20%.

Introduction

Ionic liquids are ionic compounds with melting points below 100 °C, and, as synthesized low- or non-volatile liquids and electrolytes, have found numerous industrial applications as green solvents for chemical reactions, crystallizations and extractions, and as electrolytes for batteries and energy storage devices.^{1,2}

Of timely interest, ionic liquids have also recently been studied as CO₂ capture materials,³ environmentally friendly explosives and propellant fuels.⁴ Liquid crystals, as unique ordered and

nanostructured fluids, represent another important class of soft materials. Their dynamic nature, function-integration and stimuli-responsiveness have been successfully utilized on ubiquitous information displaying devices for about half a century. For the last two decades or so, liquid crystals have also been extensively studied as mesophase semiconductors.⁵⁻¹⁵ Therefore, the synergistic hybridization of ionic liquids and liquid crystals promises new and interesting industrial and materials opportunities.

Ionic liquid crystals (iLCs)¹⁶⁻²³ are attracting much attention and are genuinely emerging as multifunctional self-assembled materials due to their natural tendency to self-organize into long-range anisotropic nanostructures with well-defined segregated ionic and electronic conducting channels, that may be used as electrolytes in Li-ion batteries, fuel cells, as well as dye-sensitized solar cells. As dynamic ordered materials, iLCs possess the best properties of both ionic liquids and liquid crystals, combining electrostatic and p-p core interactions, with the nanosegregation between alkyl chains, ionic moieties

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† Electronic supplementary information (ESI) available: Experimental techniques, synthesis, POM, TGA, DSC, ¹H and ¹³C NMR, HRMS, SAXS, DFT.

and aromatic cores.¹⁷ iLCs therefore possess tremendous potential applications such as ordered reaction media,¹⁶ anisotropic ionic^{24–26} and electronic^{27,28} conductions, and transport media,²⁹ media for alignment of single wall carbon nanotubes (triphenylene-based ionic discogens show Col_{hex} and bicontinuous cubic mesophases),^{27,30,31} applied in biological field as siRNA transfection vectors.²⁹ Essentially most iLCs so far reported, possess one or two alkyl tails connected to either a small ionic moiety or a rod-like core, and for most of them, show smectic phases,^{17,32–37} with only a few cases displaying columnar phases.^{38,39} In contrast, studies of ionic discotic liquid crystals (iDLCs) with a discotic core and displaying columnar mesophases,^{40–42} are however only just emerging, and only few examples have been reported so far. DLCs with polycyclic aromatic hydrocarbon (PAH) cores^{5–8,10,12–15} are indeed of interest since they spontaneously self-organize into columnar mesophases, and possess one-dimensional electronic charge hopping pathway along the molecular columns with fast charge carrier drift mobility. DLC semiconductors are studied as active materials in organic thin film devices, such as photovoltaic solar cells, organic light-emitting diodes, and field-effect transistors. Up to now, the design of iDLCs consists mainly in the peripheral decoration of the neutral triphenylene discotic core by pending pyridinium, ammonium, guanidinium or the emblematic imidazolium units, connected to the discotic unit through soft alkyl spacers.^{18,19,43–53} They usually show columnar mesophases near room temperature and over large temperature ranges. Inversely, imidazolium or other suitable cations may be used as connectors between triphenylene units to yield dimeric systems.^{48,50} Other systems include bis-triphenylene derivatives connected through crown ethers whose mesophases' stabilities are enhanced upon the host–guest complexation to various cations.⁵⁴ Ionic tapered^{55–57} and dendronized⁵⁸ molecular systems have also been reported with various types of counterions and found to self-organize into columnar (and cubic) mesophases. Overall, few examples of conjugated core-charged iDLCs with heterocyclic cores containing oxygen, nitrogen or sulfur atoms have been reported.^{40–42}

The synthesis of novel iDLCs is still facing big challenges, as the construction of charged heterocyclic aromatic hydrocarbons is rendered more difficult by more complex synthetic methodologies based on coupling reactions of variable efficiencies, and their extremely tedious purifications.⁴² Here, we report a simple molecular design and straightforward synthesis of the azatriphenylene molecular unit, i.e. N-heterocyclic aromatic, 2, and of the corresponding series of quaternized salts 3 and 4 (Scheme 1) with anions such as Br[−], I[−], NO₃[−], BF₄[−], PF₆[−], triflate (CF₃SO₃−TfO[−]), bis(trifluoromethylsulfonyl)-imide (Tf₂N[−]), tosylate (TsO[−]), saccharinate (sac[−]), D and L camphorsulfate (CS[−]), alkylsulfonates (C_nH_{2n+1}SO₃[−]), and alkyl-sulfates (C_nH_{2n+1}SO₄[−]). Their physical properties can be tuned by the alkyl chain length on the N-substituent (methyl and hexyl) and the overall number of aliphatic chains, as well as by the size and nature of the anion. Overall, the organic salts 3 and

4 exhibit high thermal stability, strong photoluminescence in solution and solid films, and stable columnar mesophases compared to their neutral hexa(alkoxy)triphenylenes analogues.

Scheme 1 Synthetic conditions, nomenclature and yields of azatriphenylene 2 and corresponding quaternized ionic discotic liquid crystal salts 3 and 4.

Results and discussion

Molecular design, synthetic methodology

Designing and synthesizing iDLCs possessing charged aromatic cores is slightly more challenging than replacing the side chains of a discotic LC by lipophilic fragments bearing ionic ammonium, pyridinium or imidazolium end groups.^{19,20} By analogy to triphenylene DLC, the archetype molecular structure for columnar mesogens,⁵ we considered a structurally related discogen with a positively charged core by replacement of one of the C-atom by a N-atom. Such an azatriphenylene derivative, bearing four diverging alkoxy chains, i.e. 6,7,10,11-tetrakis(hexyloxy)dibenzo[f,h]isoquinoline, can be readily obtained in two successive coupling reactions, followed by the subsequent N-alkylation to connect a fifth side-chain to promote the formation of columnar mesophases.

Within this molecular design, three structural parameters can thus be independently and simply varied, including the length of the chains (O- and/or N-alkyl chains), the type and size of the anion, to allow the tuning of the columnar mesophases symmetry, thermal stability, solubility, as well as the photo-physical properties (Scheme 1).

Keeping the above design in mind, we tested two different synthetic routes for preparing the azatriphenylene derivative **2** (Scheme 1). According to our previously reported method⁵⁹ for the synthesis of unsymmetrical substituted triphenylenes, we first prepared *o*-phenylpyridinebenzene (i.e. 4-(3',4,4',5-tetrakis-(hexyloxy)-[1,1'-biphenyl]-2-yl)pyridine) by Suzuki–Miyaura cross-coupling reaction between 2-bromobiphenyl derivative and pyridinyl-4-boronic acid. However, the following FeCl₃-catalysed oxidative intramolecular aryl–aryl coupling did not give the desired azatriphenylene **2**, possibly due to lower p-electron density of the pyridine core.⁶⁰ For an alternative synthetic route (Scheme 1), 3,4-dibromopyridine was first reacted with the readily accessible 3,4-di(hexyloxy)phenylboronic acid by Suzuki cross-coupling reaction (Scheme S1, ESI†), followed by the FeCl₃-catalysed oxidative aryl–aryl intramolecular coupling.⁵⁹

This two-steps method gave the desired azatriphenylene **2** in an overall yield of 65%. N-Alkylation of **2** with 1-bromohexane or iodomethane in hot toluene produced after 24 h the corresponding ionic discogen **3a** and **4a**, respectively, in yields greater than 80%.

The 16 ionic azatriphenylene-based salts **3b–n** and **4b–d** were obtained by anion exchange metathesis reaction of various inorganic or organic salts in dichloromethane with both precursory salts, **3a** and **4a**, respectively, and obtained in satisfactory yields (synthetic details are given in ESI†). All synthesized salts were characterized by ¹H and ¹³C NMR spectroscopy and elemental analysis (Table S8 and Fig. S8–S28 in ESI†). For all compounds of the series **3**, elemental analyses are satisfactory (with a deviation from theoretical carbon % content smaller than 0.4% for most, and just below 0.5% for **3c** and **3l**, ESI†). For compounds **4a** and **4d** of series **4** however, this deviation is slightly more substantial, by ca. 0.9–1%, which may be associated to some weight-loss occurring at an early stage, i.e. below 100 °C for **4d** (loss of a water molecule) and below 150 °C for **4a** (partial demethylation, Fig. S2, ESI†). These analyses supported the targeted molecular structures.

¹H NMR characterization

The structure and nature of the anions impact strongly the chemical and physical properties of the entire ionic liquids, and consequently those of the iLCs as well. ¹H NMR is known as an efficient spectroscopic technique to explore these various interactions between anions and cations, and particularly the hydrogen bond accepting ability, which is extremely relevant for some ionic liquids such as imidazoliums.⁶¹ For the ionized azatriphenylene compounds **3** and **4**, the chemical shift values of ¹H NMR on the aromatic core protons, essentially the displacements of the signals corresponding to both neighbored protons of the N atom of the pyridine fragment, are obviously affected by the quaternization and display strong relationships with the nature of the anion. For instance, Br[−] and I[−] have strong H-bonding forming ability with such types of protons, and consequently, their chemical shift values in compounds **3a** and **3b** (Table S8 and Fig. S1, ESI†) are large, and substantially deshielded with respect to those of **2** (Fig. 1a). In contrast, for fluorine-containing anions such as BF₄[−], PF₆[−] and Tf₂N[−] (except for the TfO[−] compound whose proton shift seems unaffected),

Fig. 1 Comparison of ¹H NMR spectra of the positively charged ionic DLCs **3** (a) and **4** (b); only aromatic regions showed for clarity; dashed lines is the chemical shift of proton H1 of **2**.

having lower H-bonding ability with azatriphenylene C–H(1) atom, the ¹H NMR spectra of compounds **3d**, **3e**, and **3f** show upfield shifts of the signals of the hydrogen nuclei instead. Chemical shift displacements of compounds containing sulfones, sulfates, sulfonates (and nitrates) are comparable to **3b**, but are still slightly deshielded with respect to signals of **2**. The same trend is observed for compounds of series **4** (Fig. 1b). These results thus coincide quite well with the trend observed in imidazolium-containing ionic liquids (Fig. 1).⁶¹

Decomposition analysis (TGA)

Humidity sensitivity and thermal stability are two important parameters for ionic liquid and thermotropic ionic liquid crystals. In particular, since salts **3** and **4** were synthesized by quaternization of the pyridine moiety, de-quaternization reaction is likely to occur on heating at high temperature by expelling the alkyl halide fragment, as previously reported.⁶²

The decomposition or de-quaternization temperatures (*T*_{dec.}, defined as the onset temperature at 5 wt% weight-loss) of the synthesized organic salts, have been determined by TGA, and are gathered in Table S1 and shown in Fig. 4 and Fig. S2 (ESI†). They decompose over a broad range of temperatures, comprised between 262 and 393 °C (temperature at 5% loss). Compounds with small sized inorganic anions, **3a–c** (Br[−], I[−], NO₃[−]) and **4a** (I[−]) exhibit the lowest thermal stability, displaying *T*_{dec.} between

262 and 269 °C, likely due to the above mentioned fast dequaternization and the subsequent release of the alkyl halide/nitrate. In contrast, **3f** and **4b**, with the same highly stable bis(trifluoromethylsulfonyl)imide anion (NTf_2^-), exhibit the highest thermal stability, with $T_{\text{dec.}}$ at 390 and 393 °C, respectively. Replacement of the bromide ion with bulkier anions such as PF_6^- , BF_4^- , TfO^- , NTf_2^- , TsO^- resulted in increasing thermal stability and high $T_{\text{dec.}}$ (>330 °C). The decomposition temperatures of the compounds with the large organic anions (i.e. alkylsulfonate, alkylsulfate, saccharinate, camphorsulfate) lie at intermediate values (295 < $T_{\text{dec.}}$ < 329 °C), consistent with reported pyridinium ionic LCs. From the experimental results listed above, the thermal stability of the iDLCs can be correlated with the nature of the anions. Indeed, due to the stronger ability of Br⁻ and I⁻ anions (and to a lesser extent NO_3^-) to form hydrogen bonding, and thus their stronger basicity, thermal dealkylation reaction is much favoured for these compounds (**3a-c** and **4a**). On the contrary, dealkylation reaction is less favoured for **3d-f** and **4b** due to the weaker interactions of BF_4^- , PF_6^- , Tf_2N^- anions with the ionic aza-core, and therefore they exhibit higher thermal stability. Therefore, the anion interaction strength determines the thermal stability of these iDLCs: the stronger nucleophile the anion, the lower thermal stability the iDLC.

Investigation of the liquid-crystalline properties of the ionic discogens (POM, DSC, SAXS)

The liquid crystalline properties of **2** and salts **3a-n** and **4a-d** were investigated by polarizing optical microscopy (POM, Fig. 2 and Fig. S1, ESI[†]), differential scanning calorimetry (DSC, Fig. S3, ESI[†])

Fig. 2 Selection of typical optical textures of some representative iDLCs, obtained after slow cooling from the isotropic liquid into the mesophases.

Fig. 3 SAXS patterns of four representative salts.

and small-angle X-ray scattering (SAXS, Fig. 3 and Fig. S4, ESI[†]). The phase transition temperatures and enthalpies are gathered in Table S2 (ESI[†]) and mesophases' parameters and indexation are given in Table 1 and Table S3 (ESI[†]). Essentially all the ionic compounds display columnar mesophases, resulting from the stacking of the flat discoid cores (Fig. S8, DFT, ESI[†]) into columns, separated from each other by the aliphatic continuum. In contrast, the neutral parent azatriphenylene **2** is non-mesomorphous

Table 1 Geometrical parameters of the mesophases of salts 3 and 4^a

Cpds	T	V _{mol} /r	Phase	Symmetry	a	b	g	A	Z	A _{mol}	h _{mol}	h _p	w _{ch}
3b	100	1301/1.07	Col _{hex}	p6mm	21.06	21.06	120	384.0	1	384.0	3.39	3.48	0.65(9)
	130	1324/1.06	Col _{hex}	p6mm	21.32	21.32	120	393.7	1	393.7	3.36	3.54	0.66(1)
3e	50	1309/1.09	Col _{hex}	p6mm	22.06	22.06	120	421.4	1	421.4	3.11	3.55	0.63(2)
	80	1332/1.07	Col _{hex}	p6mm	21.82	21.82	120	412.4	1	412.4	3.23	3.58	0.63(5)
3f	60	1456/1.14	Hex	p3m1	21.71	21.71	120	408.2	1	408.2	3.57	3.62	0.56(5)
	120	1501/1.10	Hex	p3m1	21.89	21.89	120	415.0	1	415.0	3.62	3.69	0.57(9)
	180	1547/1.07	Hex	p3m1	21.85	21.85	120	413.5	1	413.5	3.74	3.81	0.58(6)
3g	100	1498/0.99	Col _{hex}	p6mm	21.78	21.78	120	410.7	1	410.7	3.65	3.57	0.57(2)
	150	1536/0.97	Col _{hex}	p6mm	21.85	21.85	120	413.3	1	413.3	3.71	3.62	0.57(8)
	230	1598/0.93	Col _{hex}	p6mm	21.97	21.97	120	418.2	1	418.2	3.82	3.74	0.58(6)
3h	130	1394/1.03	Col _{hex}	p6mm	21.53	21.53	120	401.4	1	401.4	3.47	3.55	0.62(8)
	230	1471/0.98	Col _{hex}	p6mm	21.59	21.59	120	403.7	1	403.7	3.64	3.66	0.63(7)
3l	150	1479/1.00	Col _{hex}	p6mm	22.25	22.25	120	428.8	1	428.8	3.45	3.52	0.60(0)
	250	1561/0.94	Col _{hex}	p6mm	22.39	22.39	120	434.1	1	434.1	3.59	3.60	0.60(8)
3m	150	1563/1.01	Col _{hex}	p6mm	21.92	21.92	120	416.0	1	416.0	3.76	3.54	0.56(8)
	250	1648/0.95	Col _{hex}	p6mm	21.82	21.82	120	412.5	1	412.5	4.00	3.66	0.57(5)
3n	150	1563/1.01	Col _{hex}	p6mm	22.10	22.10	120	423.0	1	423.0	3.69	3.59	0.56(8)
	250	1648/0.95	Col _{hex}	p6mm	21.92	21.92	120	416.0	1	416.0	3.96	3.66	0.57(5)
3i	120	1680/0.97	Col _{hex}	p6mm	24.37	24.37	120	514.6	1	514.6	3.26	3.52	0.72(5)
	200	1760/0.92	Col _{hex}	p6mm	24.34	24.34	120	513.1	1	513.1	3.43	3.63	0.73(1)
3j	120	1664/0.96	Col _{hex}	p6mm	23.59	23.59	120	481.9	1	481.9	3.45	3.51	0.73(2)
	230	1775/0.90	Col _{hex}	p6mm	24.20	24.20	120	507.3	1	507.3	3.50	3.65	0.73(9)
3k	150	1516/0.96	Col _{hex}	p6mm	22.43	22.43	120	435.9	1	435.9	3.48	3.51	0.70(3)
	250	1605/0.91	Col _{hex}	p6mm	22.55	22.55	120	440.4	1	440.4	3.64	3.67	0.70(9)
4b	30	1297/1.18	Hex	p3m1	21.00	21.00	120	381.9	1	381.9	3.39	3.50	0.52(5)
	120	1356/1.13	Hex	p3m1	21.32	21.32	120	393.6	1	393.6	3.45	3.55	0.53(5)
	220	1423/1.08	Hex	p3m1	21.58	21.32	120	403.3	1	403.3	3.53	3.64	0.54(5)
4c	90	1507/1.00	Rec _{pHex}	p2mg	70.00	40.40	90	2827	6	471.2	3.20	3.50	0.69(7)
	150	1562/0.97	Rec _{pHex}	p2mg	70.50	40.70	90	2869	6	478.2	3.27	3.53	0.70(1)
4d	30	1437/1.03	Rec _{pHex}	p2mg	67.72	39.10	90	2647	6	441.2	3.26	3.38	0.69(5)
	100	1501/0.99	Rec _{pHex}	p2mg	68.38	39.48	90	2702	6	450.3	3.34	3.42	0.70(1)
	250	1637/0.91	Col _{hex}	p6mm	23.20	23.20	120	466.0	1	466.0	3.51	3.53	0.71(5)

^a T, temperature of the SAXS measurement (°C); V_{mol}, molecular volume (Å³) and r, density (g cm⁻³); phase type (Col_{hex}: hexagonal columnar phase, Hex: mesophase with hexagonal lattice, Rec_{pHex}: mesophase with rectangular lattice of pseudo-hexagonal geometry (a/b = O3)) and lattice symmetry; a, b, g: mesophases' lattice parameters (Å and Å); A, lattice area (Å²) A = a²O3/2 for Col_{hex} and Hex phases, and A = a × b for Rec phases; A_{mol}: molecular area (Å²) A_{mol} = A/Z; Z: number of columns per lattice; h_{mol}: molecular slice thickness (Å) with h_{mol} = V_{mol}/A; h_p: stacking distance (Å); w_{ch}: aliphatic volume fraction, w_{ch} = V_{ch}/V_{mol} (V_{ch}, chain volume).

and shows a sharp crystal-to-isotropic transition at 132 °C. This behaviour may be due to the conjugated action of the low number of radiating aliphatic chains and the absence of stabilizing electrostatic interactions. In order to facilitate the following discussion and comparison of the thermal behaviour and LC properties of this large collection of ionic discotic compounds, the latter were subdivided into three main groups, differentiated by the total number of aliphatic chains surrounding the p-conjugated aromatic core, summing up those covalently linked to and radiating directly from the azatriphenylene moiety, and that brought by the ion pairs. We thus distinguish sets of mesogens with 6 (3i–k), 5 (3a–h, l–n, 4c–d) and 4 diverging chains (4a and 4b), respectively; within the 5-chain systems, we can further distinguish 3 sub-groups, those with inorganic (3a–e), organic (3f–h, l–n) and lipophilic (4c–d) counterions, respectively. The overall thermal behaviour of the compounds are represented in the phase diagram (Fig. 4). (i) The three mesogens with 6 chains (3i–k), whose sixth one is brought by the lipophilic anion, behave typically as their discotic hexakis(alkoxy)triphenylene homologues, except that mesomorphic properties extend to temperatures above 200 °C in presence of ions, compared to 97 °C for the hexyl DLC reference.⁶³ The three iDLCs are indeed mesomorphous over

Fig. 4 Phase transition temperatures of iDLCs (3a, 3d and 3k: first heating cycle, 3g: crystalline range from 1st heating cycle (both in grey) and monotropic mesophase range (in cyan) from cooling cycle; all other salts: 2nd heating cycle). Red lines correspond to decomposition temperatures.

large temperature ranges (120–150 °C): the sulfonate derivative 3j has a slightly higher clearing temperature (ca. 240 °C) than its homologous dodecyl sulfate 3i (ca. 210 °C). In contrast, the

derivative with the shorter chain of same length as the alkoxy substituents (3k) clears at much higher temperature, up to nearly 300 °C, following the trend reported for symmetrical vs. unsymmetrical hexakis(alkoxy)triphenylenes.⁶⁴ On cooling from the isotropic liquid, they display birefringent fan-shaped textures within large homeotropic areas, characteristic of the hexagonal columnar phase (Fig. 2 and Fig. S1, ESI†). DSC also reveals an additional phase transition at lower temperature, undetectable by POM. The SAXS patterns of the 3 compounds were recorded at various temperatures (Fig. S4, ESI†), and all exhibit the characteristic features of a two-dimensional columnar hexagonal phase, in agreement with POM observations. In the wide-angle range, two broad scattering signals were systematically present, emerging respectively from the average lateral distances between molten chains (h_{ch} , $\approx 4.5\text{--}4.7$ Å) and from the stacking periodicities between the flat mesogenic cores piled into columns (h_p , $\approx 3.5\text{--}3.7$ Å); although the broadness of the latter signal indicates that the nearly orthogonal stacking is short-range. In the small-angle range, the presence of one strong first-order reflection (10) and up to three weakly-intense supplementary reflections, according to spacing ratios 03, 2, 07 and indexed as (hk) = (11), (20) and (21) (Table S3, ESI†), confirms in all cases the formation of long-range two-dimensional hexagonal lattice with one single column, with well-defined interfaces between the piled cores and the surrounding chains. The low-temperature phase(s) labelled as M (and M') detected by DSC, showed very similar SAXS patterns (but with supplementary mid- and wide-angle rising peaks, displacement of the wide-angle diffusion to smaller angles, and/or broadening of the fundamental reflection) suggesting that they must retain the main features of the above fluid mesophase, with locally preserved columnar structuration. These intermediate stable states likely result from the stiffening and even partial crystallization of the aliphatic chains concomitant to an enhanced stacking due to some possible slight re-organization of the counterions around the aromatic cores.

(ii) All compounds with 5 chains and small inorganic anions (3a–e), but salts 3a (Br⁻) and 3d (BF₄⁻), exhibit enantiotropic mesophases, over small temperature ranges (Table S2, ESI†), with a maximum clearing temperature of 137 °C for 3b. The reduction to five radiating chains combined with small anions results in the drastic diminution of phase stability by more than 100 °C with respect to the previous series. As observed by POM, the mesomorphic compounds displayed a wide range of characteristic optical textures of hexagonal columnar mesophases e.g. fan-shaped, long linear defects and large homeotropic domains (Fig. 2 and Fig. S1, ESI†). The absence of LC properties for 3a and 3d might be due to the peculiarities of both Br⁻ and BF₄⁻ anions.¹⁷ For salt 3a, only one transition was seen during the first heating run corresponding to melting from the crystalline state into the isotropic liquid. On cooling from the isotropic liquid, no sign of crystallization was detected, even at room temperature after several weeks, meaning that this salt behaves as a true ionic liquid. For 3d, the absence of LC properties, may be due to tendency of BF₄⁻ to have closer contact with the N-atom, even to intercalate between successive discs,

disturbing substantially the p–p stacking of the aromatic cores into columns. SAXS measurements, recorded for 3b and 3e only (3c showed extensive decomposition upon exposure to the X-ray beam while in the mesophase), confirmed the self-assembling into columnar hexagonal mesophases (Col_{hex}), as characterized by the two strong wide-angle scattering signals, h_{ch} (≈ 4.5 Å) and h_p ($\approx 3.5\text{--}3.6$ Å), and by the intense small-angle fundamental reflection (10). Similarly to the 6-chain compounds, a low-temperature mesophase, M, was also detected by DSC, which similarly retains the principal organization of the Col_{hex} mesophase, as revealed by SAXS (Fig. S4, ESI†).

(iii) The ion exchange with the more voluminous triflate (3h), bis(trifluoromethylsulfonyl)imide (3f), tosylate (3l), saccharinate (3g) and camphorsulfate (3m, 3n) anions resulted overall in a substantial enhancement of the mesomorphic temperature ranges and phase stabilities, similarly to the results obtained after the substitution with lipophilic anion in the 6-chain derivatives (3i–k). The congestion of the saccharinate moiety however nevertheless destabilizes the mesomorphism in 3g, which only occurs on cooling from the isotropic liquid (monotropic behaviour). Apart for 3g and the Tf₂N compound 3f, which has the lowest clearing (below 200 °C), the behaviour of the other terms of this series is more or less constant with clearing temperatures fluctuating around 250 ± 30 °C, the higher ones for the camphorsulfate derivatives. Optical textures presented broken fan shapes (3f, 3h) hexagonal dendritic domains and fernlike texture (3g), and fan-shaped defects (3l,

3m and 3n) and systematically large homeotropic domains for all, all characteristic features of the hexagonal columnar phase (Fig. 2 and Fig. S1, ESI†). The SAXS patterns of 3g, 3l, 3m and 3n turned out to be similar and displayed classical patterns of a hexagonal columnar structure, as for the 6-chain compounds discussed above. All presented the broad scattering h_{ch} ($4.5\text{--}4.8$ Å) and the semi-diffuse scattering h_p ($3.5\text{--}3.7$ Å) signals. In the small-angle range, a very intense fundamental reflection (10) was systematically observed, along with up to 4 higher-order reflections, indexed as (11), (20) and (21), for 3g and 3l, or only one higher-order reflection, indexed as (21), for 3m and 3n. As observed above, the low-temperature mesophase M is no more fluid and is a structural reminiscence of the hexagonal phase. The two compounds with highly-fluorinated counterion (3f, 3h) however showed SAXS patterns of different appearance, though still in agreement with hexagonal symmetry. SAXS pattern of 3h (Fig. 3) revealed a sharp but weakly intense fundamental (10) reflection, along three weak additional peaks ((11), (20), and (21)), the broad scattering (h_{ch}) and the only slightly broadened and very intense periodicity (h_p) corresponding to a regular and cohesive stacking of the cores. This pattern is still in agreement with classical Col_{hex} configuration, i.e. with columns of stacked mesogens at lattice nodes, separated by peripheral continuum of molten chains. The only particularity is that the TfO counterions distribute randomly around columns with the high electron-density CF₃ groups protruding in the aliphatic continuum. The average electronic density of the continuum is therefore elevated and the contrast with columns thus reduced, which explains the exhaustion of the (10) reflection. For 3f, the

fundamental reflection (10) and the first higher-order reflection (11) even totally vanished in the SAXS pattern, leaving only a set of 4 small-angle, sharp but weakly intense, high-order reflections, (21), (30), (22) and (31), the last two only seen at low temperature. The missing low-angle reflections, together with the maintenance of a single-column lattice area, reveal that the counterions are not any more randomly distributed but generate a peak of electronic density at defined positions between columns. Indeed, triflimide is rather voluminous, and actually corresponds to almost 2/3 of the azatriphenylene disc volume, so that the stacking process necessarily involves interactions between counterions. Consistently, a scattering signature of the packing within triflimide domains (h_{NTf_2}) is seen in the wide-angle region (maximum at roughly 5.5 Å), next to the scattering signals of triphenylene stacking (h_p) and molten chain packing (h_{ch}). This configuration has more structural features than a genuine Col_{hex} mesophase and was hence assigned to a “meso-phase with two-dimensional hexagonal structure” (Hex).

(iv) The last two compounds with 5 chains, 4c and 4d, show similarly wide-temperature range mesophases, from room temperature up to 250 °C and 280 °C, respectively. Their optical textures were uncharacteristic (Fig. S1, ESI[†]), and not sufficiently specific to identify the mesophase. Columnar-like mesomorphism was confirmed by SAXS (Fig. 3 and Fig. S4, ESI[†]). The wide-angle range was similar as described above (broad h_{ch} scattering and intense and only slightly broadened h_p peak) in agreement with cohesive and regular stacking of the cores into columns. The various sharp reflections measured in the small-angle range were indexed according to a non-centred rectangular symmetry of pseudo-hexagonal geometry, i.e. with lattice parameter ratio $a/b = \sqrt{3}$ (Table S3, ESI[†]). The missing fundamental reflections (11)/(20) and the large size of the lattice indicate a multisegregated arrangement with several columns per lattice, assigned to a “mesophase with rectangular pseudo-hexagonal structure” (Rec_{pHex}). On increasing the temperature above 118 °C, the small-angle part of the SAXS pattern of 4d transformed, in agreement with the transition into another mesophase (as observed by DSC). The small reflection (21) of the low-temperature phase disappears, allowing the indexation of the intense reflection as (10) and the small one as (11) of a hexagonal lattice, and thus to the formation of a Col_{hex} phase.

(v) The last mesogens of this series of compounds, 4a and 4b, possess only 4 chains. Unlike the neutral precursor, both display wide-range mesophases, with clearing above 200 °C. The textures of 4a and 4b were rather uncharacteristic (Fig. S1, ESI[†]) and the nature of the mesophases could not be established at this stage by this technique only. Compound 4a could unfortunately not be analysed further due to extremely fast degradation upon exposure to X-ray sources, even at low temperatures (See TGA, Fig. S2, ESI[†]), and thus the mesophase could not be ultimately identified. The SAXS pattern of 4b was however almost identical to that of the other triflimide-containing salt 3f discussed above. Indeed, the SAXS pattern revealed a set of 5 small-angle high-order reflections of a hexagonal lattice, sharp and weakly intense, (11), (21), (30), (22) and (31), the last two disappearing upon temperature increase. In addition

to the broad scattering of the molten chains (h_{ch}) and the intense reflection corresponding to the stacking periodicity (h_p) that associated to the bulky triflimide moiety (h_{NTf_2}) was clearly seen. The missing fundamental reflection (10), the lattice size and the presence of h_{NTf_2} therefore confirm the same three-domain Hex structure for 4b as for 3f. The supramolecular organization of all the compounds will be discussed in the next section.

Supramolecular organization in the mesophases

Most compounds with 5 and 6 side-chains, and in particular those with a longer chain on the quaternized azatriphenylene cores (Atp⁺) and relatively small counterions, self-assemble in Col_{hex} mesophases. The average structure consists in $p6mm$ arrangement of cylindrical columns spaced by a continuum (Fig. 5), which implies that the nearly-discoid rigid cores adopt various orientations along the stacking direction to allow a homogeneous distribution of the aliphatic chains and counter-anions in their periphery. The values of h_{mol} (columnar slice thickness calculated from the ratio between the molecular volume, V_{mol} , and the molecular area, A_{mol} , Table 1) for 3f–h, 3l–n, 3i–k are very comparable to h_p (with a maximum discrepancy of ± 0.2 Å), and compatible with the nearly orthogonal stacking of the cores within the columns (i.e. without tilt or only small tilt angles of the cores due to thermal fluctuations). These iDLCs therefore self-assemble just in the same way as the parent hexa-substituted DLCs, except that the aliphatic continuum incorporates the counterions. The ionic interactions with Atp⁺ columns however considerably reinforce the cohesion of the stacking and lead to mesomorphic range extensions between 100 and 200 °C relatively to reference DLCs. For series 4, the self-assembly process yields different structures, obviously

Fig. 5 Schematic views of the likely supramolecular organizations.

because the replacement of the longer chain by a methyl group authorizes neighbouring columns to move closer. For 4c–d, this proximity leads to a large-size lattice Rec_{pHex} phase following the bridging of the columns by the counterions and the arrangement of the so-formed clusters into a rectangular, non-centred lattice. Lattice size, pseudo-hexagonal geometry and intensity variation in the reflection series indicate a herringbone alignment of clusters of 3 bridged columns, the likely arrangement of p2mg symmetry being schematically represented in Fig. 5. The structural features are essentially the same for the OSO_3^- (4c) and SO_3^- (4d) anionic heads, but the cohesion of the clusters are considerably lower for SO_3^- as they dissociate at 118 °C on crossing the transition to the Col_{hex} phase. The Rec_{pHex} phase of 4c is on the contrary maintained up to the clearing point around 250 °C. The reason for this early dissociation of SO_3^- -bridged clusters might be the smaller size of the anion, which increases steric constraints from crowded chains.

In any event, the anion size is determinant for the supra-molecular organization, and 3f/4b with the bulkier NTf_2^- give a structure, which is different from the other terms of the series. Triflimide is indeed too bulky anion to be drawn in the aliphatic periphery as typical in series 3 or to bridge neighbouring columns into compact clusters as observed for 4c–d. Instead, the anions interact and self-assemble to individual domains, forming a multi-segregated arrangement with intermingled triphenylene columns and molten chains zones. Thanks to the favourable stoichiometry and partial volume ratios, this structure complies with the ideal case of a honeycomb-like lattice with alternation of triflimide domains and AtpH columns at lattice nodes and molten chains zones at lattice centres (Fig. 5). With respect to Col_{hex} , this Hex structure preserves the hexagonal geometry and the single-column lattice periodicity, but the symmetry is reduced to p3m1 . It should be noticed that the longer chain or the methyl group on AtpH does

not drive the self-assembling as for the other terms of the series;

there is only a small impact on mesomorphic range width due to the swelling of aliphatic zones at honeycomb centres.

Photophysical properties of azatriphenylene and quaternized ionic discotic liquid crystal salts derivatives – UV/Vis absorption and photoluminescence properties

The optical properties were studied by UV-Vis absorption and photoluminescence spectroscopy in dilute THF solutions and in thin films (Table 2 and Fig. 6). Absorption spectra for all compounds are given in Fig. 6a. As can be seen, in dilute solutions ($10^{-5} \text{ mol}\cdot\text{L}^{-1}$), the absorption spectra of all the ionic compounds are fully superimposable in the UV-Vis range, whatever the type of counteranion and the number and length of the side-chains, and show a unique strong absorption broad band with a maximum at 292 nm, originated from the p-p^* transition (see DFT calculations in ESI[†]), typical of charged dibenzo[f,h]isoquinoline species. Upon quaternization, the absorption of 2 is then redshifted by about 20 nm (Table 2).

Whereas 2 shows blue fluorescence in THF solution, all the salts exhibit yellow fluorescence (Fig. 6 and Fig. S5, ESI[†]) with maxima centered around 525–533 nm. These minor changes imply that the excited states of the compounds are not greatly affected by anions and the length of the N-substituents. The fluorescent efficiency (quantum yield, QY) was measured with solution concentration of $1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ in THF for all compounds: 2 displayed high quantum yields, about 75% (at an excitation wavelength of 310 nm). Salt 3a displays the lowest quantum yield of emission, with an efficiency of about 2% (at 335 nm), whereas salt 3d shows the highest photoluminescence, with an efficiency of about 22% (at 360 nm).

The fluorescent properties of thin film were also studied by using solution-cast films from THF onto quartz plates (Fig. S6, ESI[†]). Each of them with the exception of 4a and 3b showed one broad and intense peak maxima centered between 500 and 549 nm when excited at 335 nm (Fig. 6). The light-emission

Table 2 Photo-physical properties of the synthesized azatriphenylene 2 and its salts 3 and 4^a

Cpds	I_{abs} (nm)	ϵ ($\times 10^4$, L mol cm^{-1})	I_{em} solution (nm)	I_{em} film (nm)	Quantum yield QY ^a [%]
2, D	275	10	397	—	75.3
3a, [HexD ⁺][Br ⁻]	292	10	529	537	2.0
3b, [HexD ⁺][I ⁻]	292	10	530	—	1.7
3c, [HexD ⁺][NO ₃ ⁻]	292	10	529	543	21.3
3d, [HexD ⁺][BF ₄ ⁻]	292	9.98	527	546	21.8
3e, [HexD ⁺][PF ₆ ⁻]	292	10	533	547	20.0
3f, [HexD ⁺][Tf ₂ N ⁻]	292	9.96	531	538	19.3
3g, [HexD ⁺][Sac ⁻]	292	10	528	533	17.9
3h, [HexD ⁺][TfO ⁻]	292	9.99	529	509	21.5
3i, [HexD ⁺][C ₁₂ H ₂₅ OSO ₃ ⁻]	292	10	526	520	20.3
3j, [HexD ⁺][C ₁₂ H ₂₅ SO ₃ ⁻]	292	10	528	504	14.6
3k, [HexD ⁺][C ₆ H ₁₃ SO ₃ ⁻]	292	10	526	520	17.6
3l, [HexD ⁺][TsO ⁻]	292	10	527	500	15.3
3m, [HexD ⁺][L-CS ⁻]	292	9.94	531	516	18.7
3n, [HexD ⁺][D-CS ⁻]	292	9.96	532	520	20.6
4a, [MeD ⁺][I ⁻]	292	10	533	—	3.0
4b, [MeD ⁺][Tf ₂ N ⁻]	292	10	536	549	19.2
4c, [MeD ⁺][C ₁₂ H ₂₅ OSO ₃ ⁻]	292	10	525	529	22.4
4d, [MeD ⁺][C ₁₂ H ₂₅ SO ₃ ⁻]	292	9.98	533	526	18.4

^a Fluorescence spectra were measured at $I_{\text{exc}} = 335 \text{ nm}$. Fluorescence absolute quantum yield of salts was measured with solution concentration of $1 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$ in THF excited at 360 nm (neutral azatriphenylene 2 excited at 310 nm).

Fig. 6 (a) UV/Vis absorption spectra; (b) photoluminescence in dilute solution; (c) photoluminescence in thin-films; (d and e) selected photoluminescence spectra and photographs in thin-films of two typical compounds; the photographs were taken under UV light (365 nm) irradiation in the thin-films at room temperature. 3l (TsO⁻, 500 nm), 3e (PF₆⁻, 547 nm).

from 4a and 3b was too weak to be measured because of the occurrence of quenching. The thin film emission spectra of some compounds displayed a red shift, when compared with those of solution spectra, indicating more ordered structures formation in the stacking of aromatic rings in the solid states, whereas some compounds displayed a blue shift, when compared with their emission in solution. Emission from solid films are far more depending on the intermolecular aggregation behaviour determined here by the anion size and geometry, and the strength of electrostatic interactions. These results support p-p-like aggregation of the ionic azatriphenylene core in thin films. This unexpected anion selectivity could be leveraged in various potential applications as organic fluorescent sensors and opto-electronic materials (Fig. 7).

These original photophysical results also revealed that neutral dibenzo[*f,h*]isoquinoline 2 and corresponding ionic dibenzo[*f,h*]isoquinolin-2-ium derivatives 3 and 4 represent a new and interesting type of luminophore and luminescent organic salts, constituted of p-conjugated heterocyclic aromatic hydrocarbon ionic unit, with absolute emission quantum yields above 20%.

Conclusions

A novel heterocyclic azatriphenylene polycyclic aromatic hydrocarbon 2 was obtained in good yields from readily accessible precursors by Suzuki–Miyaura cross-coupling reaction and FeCl₃ oxidative Scholl cyclodehydrogenation reaction. Quaternization of 2 by metathesis reaction with various salts, led to a collection of 18 ionic DLCs. POM, DSC and SAXS results revealed that most salts exhibit broad temperature range of p6mm-Col_{hex} meso-phase; two compounds of the series 4 exhibit a mesophase with an arrangement of column and counterion clusters according to a rectangular lattice of pseudo-hexagonal geometry (i.e. $a/b = 0.3$) and p2mg symmetry, whereas the triflimide-containing compounds give a mesophase with a honeycomb-like lattice of p3m1 symmetry (Hex). The thermal stability of these ionic DLC is high in most cases, with decomposition temperatures between 262–393 °C and a strong anion-dependence. The optical properties displayed UV/Vis absorption and anion-selective luminescence with wavelength in the range 500–550 nm, with quantum yield as high as 20%, while azatriphenylene 2 as a novel blue luminophore displays absolute quantum yield of 75%. Azatriphenylene-based ionic compounds have the potential to become a workhorse of ionic DLCs, and this scaffold can be further tuned by ionic self-assembly for polarizing luminescence, anionic sensors, and ordered ion and electron transport materials.

Fig. 7 Comparison of the photoluminescence in thin films and solution for compounds of series 3, as a function of the counterion X.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was financially supported by the National Natural Science Foundation of China (NSFC, Fund numbers: 21772135, 51273133, 51773140). BD and BH thank CNRS and University of Strasbourg for support.

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