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Mesomorphism Modulation of Perfluorinated Janus Triphenylenes by Inhomogeneous Chain Substitution Patterns†

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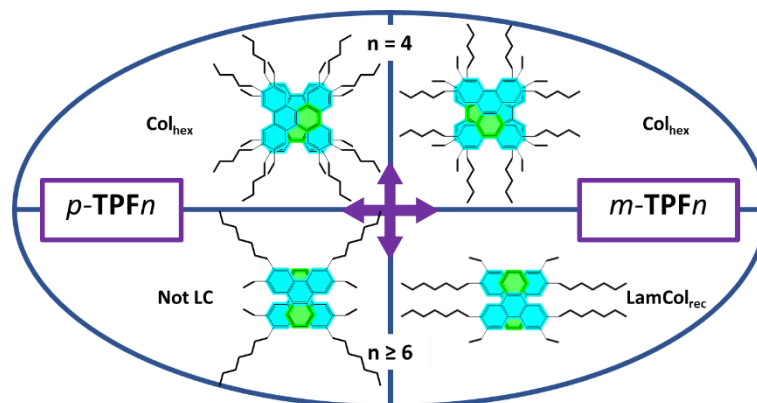
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Nucleophilic 2,2'-dilithium-5,5'-dialkoxy-4,4'-dimethoxybiphenyl derivatives and their isomeric 2,2'-dilithium-4,4'-dialkoxy-5,5'-dimethoxybiphenyl homologs were reacted with electrophilic perfluorobenzene to yield 7,10-dialkoxy-1,2,3,4-tetrafluoro-6,11-dimethoxytriphenylene (*p*-TPFn) and 6,11-dialkoxy-1,2,3,4-tetrafluoro-7,10-dimethoxytriphenylene (*m*-TPFn), respectively. The compounds display hexagonal columnar (Col_{hex}) or lamello-columnar (LamCol_{rec}) phase depending on the topology of the aliphatic periphery (i.e. chain-length and symmetry of the chain substitution pattern).



Abstract Two isomeric series of compounds with “inverted” chains’ substitution patterns, 7,10-dialkoxy-1,2,3,4-tetrafluoro-6,11-dimethoxytriphenylene and 6,11-dialkoxy-1,2,3,4-tetrafluoro-7,10-dimethoxytriphenylene, labelled respectively *p*-TPF*n* and *m*-TPF*n*, and two non-fluorinated homologous isomers, 3,6-dibutoxy-2,7-dimethoxytriphenylene and 2,7-dibutoxy-3,6-dimethoxytriphenylene, *p*-TP4 and *m*-TP4, respectively, were synthesized in three steps and obtained in good yields by the efficient transition-metal-free, fluoroarene nucleophilic substitution via the reaction of appropriate 2,2’-dilithium biphenylenes with either perfluorobenzene, C₆F₆, to yield *p*-TPF*n* and *m*-TPF*n*, or *o*-difluorobenzene, C₆H₄F₂, for *p*-TP4 and *m*-TP4, respectively. The single-crystal structures of *p*-TPF4, *m*-TPF4 and *p*-TP4, unequivocally confirmed that the cyclization reactions occurred at the expected positions, and that the fluorinated molecules stack up into columns with short separation, a propitious situation for the emergence of columnar mesophases. The mesomorphous properties were found to be greatly affected by both chains’ length and positional isomerism: a Colhex phase is found for *p*-TPF4 and *m*-TPF4, but mesomorphism vanishes in *p*-TPF6, and changes for the isomeric homologs *m*-TPF*n*, with the induction for $n \geq 6$ of a lamello-columnar phase, LamCol_{rec}. As expected, both non-fluorinated compounds are deprived of mesomorphism. These compounds emit blue-violet colour in solution, independently of the chains’ substitution pattern, and the absolute fluorescence quantum yields can reach up to 46 %. In thin films, fluorescence is slightly redshifted.

Keywords: Triphenylene, discotic liquid crystal, constitutional isomerism
arene-perfluoroarene interactions, nucleophilic substitution reaction of fluoroarene S_NAr, fluorescence, crystal structure

Introduction

The field of polycyclic aromatic hydrocarbons (PAHs) continues to elicit considerable interest for the display and organic electronics industries because of their remarkable electrical, optical, and surface properties.^[1-3] In general, PAHs such as picenes, acenes,^[4] triphenylenes (TP),^[5] pyrenes,^[6] coronenes,^[7] etc.... equipped with an appropriate number of peripheral aliphatic chains can spontaneously self-assemble into liquid crystalline phases, i.e. into ordered but still mobile supramolecular assemblies, which is important for facilitating wet device manufacturing processes.^[8] Among the many possible supramolecular organizations that can be formed in liquid crystals, columnar mesophases are of great interest^[1-8] for applications in organic photovoltaic materials (OPV), field-effect transistors (OFET), organic light-emitting diodes (OLED), sensing,^[8-10] as potentially conducive to the creation of efficient one-dimensional charge transport channels. An important motivation for ongoing research into discotic PAHs, beyond the creation of new and original molecular structures, is the increase in charge mobility rates, closely linked to the shortening of stacking distance and the increase in molecular order within the columns of these columnar mesophases.^[11-18] Most strategies mainly involve introducing chemical alterations around the aromatic cores by grafting various functional peripheral groups (e.g. halogen, cyanide, isocyanide, thiocyanate, nitro groups),^[19] extending the aromatic cores and/or changing the nature (hydrophobic, hydrophilic, fluorophilic, ...),^[20] the length and the topology (linear, branched, cyclic ...) of the lateral chains.^[21] Note that many other interesting characteristics such as transition temperatures, solubility/miscibility, and thermal/chemical stabilities, ... can be also modified at the same time. However, modifying the periphery by changing the number of chains and/or the symmetry of the chain substitution pattern has rarely been considered.^[22-24]

Since the 1960s, great progress has been accomplished in methods for synthesizing PAH liquid crystals and, in particular, of TP derivatives.^[5,13] An important breakthrough was the one-step oxidative trimerization reaction using FeCl₃ or VOCl₃ oxidants to prepare symmetrically substituted TP directly from *o*-dialkoxybenzene or unsymmetrical substituted TPs from 3,3’,4,4’-tetraalkoxybiphenyl and 1,2-dialkoxybenzenes,^[25-27] which opened up many new possibilities for ring extension and symmetry variation. In the same year, a class of cyano-functionalized TP derivatives were efficiently synthesized by Williamson synthesis and Suzuki coupling using dihydroxybenzene as raw material.^[28-30] Other advanced synthetic methodologies were reported for the preparation of unsymmetrical TP derivatives by Yamamoto coupling reaction,^[31,32] or by combined Suzuki coupling and Scholl intramolecular cyclization to prepare a variety of extended fused TP disc-shaped liquid crystals (DLCs),^[15] which showed excellent carrier migration rate (up to 10⁻²cm²V⁻¹s⁻¹). Recently, original extended TP-based compounds such as trinaphthylenes,

dibenzo[*f,j*]phenanthro[9,10-*s*]picenes, benzo[*c*]naphtho[2,1-*p*]chrysenes and benzo[*c*]naphtho[2,1-*l*]phenanthro[3,4-*g*]chrysenes as potentially interesting semiconducting DLCs were prepared in good yields by simple electrochemical reductive trimerization and cross-couplings nickel-catalyzed reactions from easily accessible precursors.^[33] However, although these methods can yield a great diversity of TP derivatives with complex molecular architectures relatively simply and in high yields, they may require expensive and/or toxic catalysts, harsh reaction conditions (anhydrous solvent and oxygen-free, precise/high temperature control) and expensive raw materials. It is therefore necessary to develop other, more environmentally-friendly, high-yield methods for their synthesis from simple, cheap and available raw materials, under mild reaction conditions in order to reduce costs and the production of toxic waste, improve carbon footprint and achieve large-scale synthesis.

The presence of high aliphatic content (long and numerous chains) around the aromatic nuclei, although essential for the emergence of mesomorphism, can on the contrary impair the performance of the materials with, for example, a significantly reduced mobility rate, photoelectric and optical properties. On the other hand, when designed with a low aliphatic content, mesomorphism can be suppressed or transition temperatures can be too high. A compromise must therefore be found to design new molecular systems with a reduced aliphatic volume fraction, but without suppressing their mesomorphic properties.^[23,24]

The recent observation that mesomorphism could still be induced in some fluorine-containing triphenylenes bearing only 4 peripheral chains,^[34-36] as low as methoxy,^[36] albeit with high transition temperatures, or in the tailless homologous derivatives,^[37] is highly attractive in this respect. We thus propose here the synthesis of new triphenylene compounds based on this simple fluorine-containing molecular platform but with an inhomogeneous chains' substitution pattern, i.e. *p*-**TPF n** and *m*-**TPF n** , designed to promote mesomorphism but at accessible transition temperatures. These new compounds were easily synthesized in three steps and obtained in high yields by nucleophilic substitution reaction; their fluorine-free counterparts, *p*-**TP4** and *m*-**TP4**, similarly synthesized, were also prepared for comparison. Their thermal, mesomorphic and optical properties are reported, and discussed on the basis of the chains' substitution pattern.

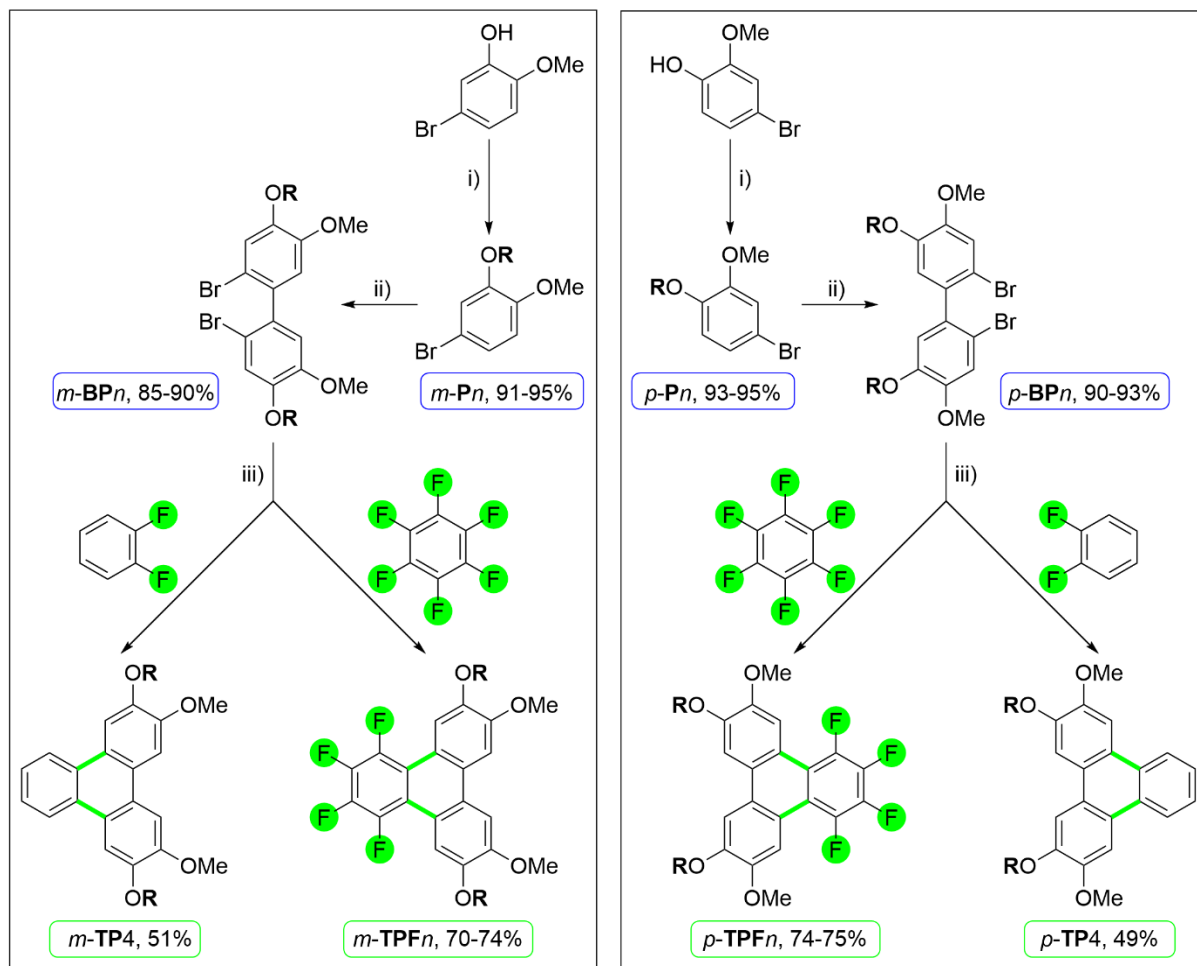
Results and Discussion

Synthetic methodology

The design of novel liquid crystal molecules with better performances is always a major challenge. The introduction of electron-withdrawing groups (-F, -CN, etc.) can improve the shortcomings of traditional disc-shaped liquid crystal materials, among which fluorine atoms stand out among many substituted groups with their potential application values, and also inject a new vitality in the design of organic liquid crystal molecules.^[38-52] Zhao et al.^[38-40] synthesized fluoro-TP disc-shaped liquid crystal derivatives by Suzuki-Miyaura cross-coupling reaction, and it was found that these compounds presented hexagonal columnar phase (Col_{hex}), with increasing clearing temperatures concomitantly with the increase of the number of fluorine atoms, indicating that the introduction of fluorine atoms promoted long-range and efficient molecular stacking into stable columnar phases. In 2021, Vieira et al.^[53] prepared a series of disc-shaped liquid crystal molecules with a central triazine nucleus, and found that the introduction of fluorine atoms also significantly improved the liquid crystal performances (stability, liquid crystal phase range). Thus, the substitution of aromatic cores by fluorine atoms may change drastically the electronic properties of the π -conjugating systems,^[54] while the non-covalent arene-perfluoroarene intermolecular interactions induced likely affect their supramolecular architectures and organizations.^[34-36,48,54]

For the synthesis of these symmetrical fluorine-containing TP molecules (Scheme 1) with "inverted" chain-substitution patterns, namely *p*-**TPF n** and *m*-**TPF n** , 2,2'-dibromo-5,5'-dialkoxy-4,4'-dimethoxybiphenyl derivatives, *p*-**BP n** ($n=4, 6$), and their isomeric homologs, 2,2'-dibromo-4,4'-dialkoxy-5,5'-dimethoxybiphenyls, *m*-**BP n** ($n=4, 6, 8, 10$), were first synthesized by the highly selective Scholl oxidative homocoupling reaction directly from the corresponding 4-bromobenzene derivatives, *p*-**P n** and *m*-**P n** , respectively.^[34,35] Both *p*-**BP n** and *m*-**BP n** were reacted with butyl lithium^[55-57] to yield the corresponding dilithium intermediates, which were then immediately reacted with perfluorobenzene (C₆F₆) to yield the target fluorinated compounds, *p*-**TPF4/6** and *m*-**TPF4/6/8/10**, or with 1,2-difluorobenzene (*o*-C₆H₄F₂) to yield the two non-fluorinated homologs, *p*-**TP4** and *m*-**TP4**, respectively.

This synthesis route is simpler than standard used methods such as Suzuki cross-coupling reaction,^[58] Diels-Alder cycloaddition reaction,^[59] or photocyclodehydrofluorination (PCDHF),^[36,37] as only two major steps are necessary, the reaction conditions are milder i.e. no need of expensive metal catalysts and oxygen-free environment, the reagents used are cheap, and easily accessible, and the compounds easy to purify. Furthermore, the intermediates and target products are easily separated and purified, and obtained in yields greater than 70%. The synthetic route and yields are shown below in Scheme 1, and the synthesis of the intermediates is detailed in the Supporting Information, along with their complete characterization by elemental analysis, ¹H, ¹³C, ¹⁷F-NMR and mass spectroscopy.



Scheme 1. Synthetic route, nomenclature and yields of the isomeric Janus-like TP discogens, *p*-TPFn, *m*-TPFn, *p*-TP4 and *m*-TP4 (and intermediates); $R=C_nH_{2n+1}$, with $n=4, 6, 8, 10$. i) RBr, K_2CO_3 , DMF, $90^\circ C$; ii) $FeCl_3$, CH_3NO_2/CH_2Cl_2 , rt; iii) *n*-BuLi, THF, $-78^\circ C$.

Single crystal X-ray analysis

Single crystals of *p*-TPF4, *m*-TPF4 and *p*-TP4^[60] suitable for X-ray diffraction analysis were obtained by slow evaporation of a chloroform and methanol mixture. The molecular structures and molecular packings are shown in Figures 1 and S43-S48, and all crystallographic parameters are gathered in Tables 1 and S1-S12. The crystal structures unequivocally reveal that the S_NAr reactions between the dilithio-biphenylenes and hexafluorobenzene (for *p*-TPF4, *m*-TPF4) or 1,2-difluorobenzene (for *p*-TP4) worked and occurred at the expected positions. They also show the planarity of the π -conjugated systems of the fluorinated triphenylenes, which is unaffected by the presence of the fluorine atoms. The crystal unit cells are different in the three cases due to the alkoxy chains' positional isomerism and the interplay of intramolecular hydrogen bonds and arene-fluoroarene intermolecular interactions which cause huge changes in the molecular arrangements. Thus, *p*-TPF4 crystallizes in the orthorhombic *Pbca* space group, with 8 molecules per crystal unit cell, whereas isomeric *m*-TPF4 crystallizes in the monoclinic *P2₁/c* space group; *p*-TP4 crystallizes in the triclinic *P1* space group (Table 1). The crystal structures show numerous intramolecular hydrogen bonds between the

electronegative F atoms and hydrogen atoms of the aromatic ring with distances of ca. 2.036 Å and 2.016 Å, respectively for *p*-TPF4 and *m*-TPF4, and larger intermolecular distances in the range 3.3369 Å and 3.3584 Å, respectively for *p*-TPF4, *m*-TPF4 and 3.41 Å for *p*-TP4.

Molecules of *p*-TPF4 stack into columns parallel the *b*-axis, with a slight orientational shift with respect the *c*-direction. Furthermore, the columns lie into antiparallel rows along the *a*-axis, with a change of the direction every $a/2$, but with small separation between the layers (Figure 1, green arrows). In such an arrangement, intermolecular fluoroarene-arene interactions are strong within the columns but not between columns.

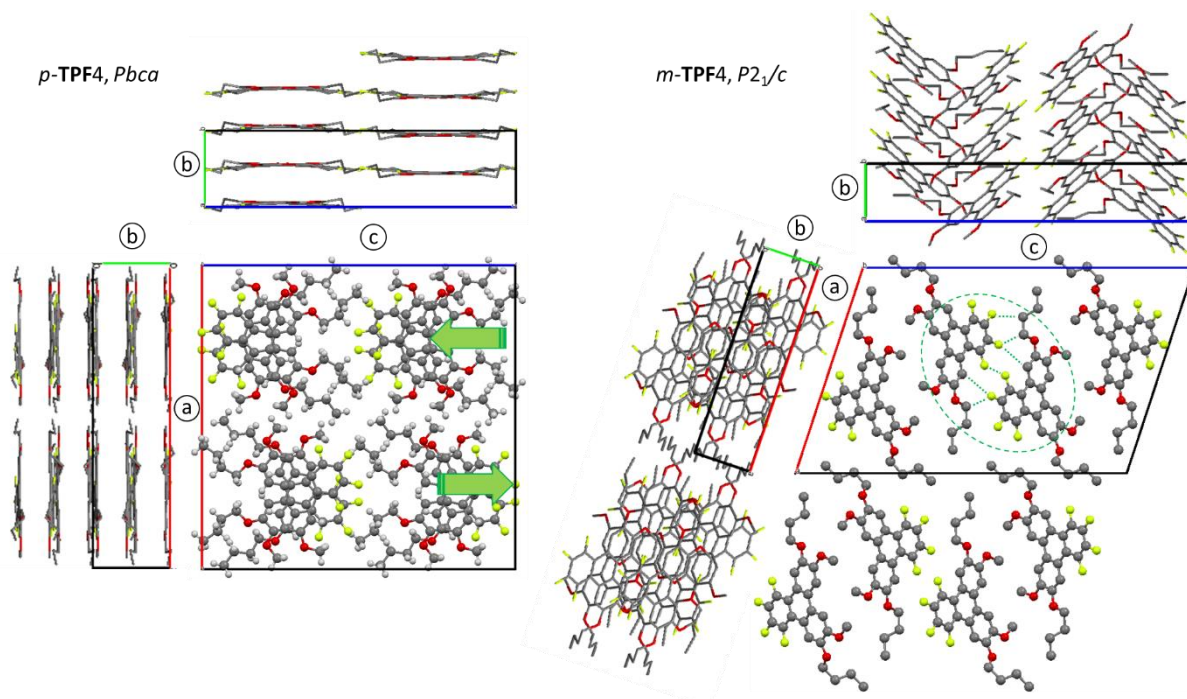


Figure 1. Single crystal structures and molecular packings of *p*-TPF4 and *m*-TPF4, viewed along the crystallographic axes.

Table 1. Crystallographic parameters of *p*-TPF4, *m*-TPF4 and *p*-TP4.

Crystal lattice parameters	<i>p</i> -TPF4	<i>m</i> -TPF4	<i>p</i> -TP4
$a/\text{Å}$	26.4574(6)	18.5810(3)	5.0982(2)
$b/\text{Å}$	6.6881(2)	4.72920(10)	12.0989(5)
$c/\text{Å}$	27.2468(8)	28.4263(3)	19.6753(7)
$\alpha/^\circ$	90	90	105.067(3)
$\beta/^\circ$	90	108.1740(10)	91.608(3)
$\gamma/^\circ$	90	90	90.488(3)
$V/\text{Å}^3$	4821.3(2)	2373.30(7)	1171.28(8)
Z	8	4	2
Space group	<i>Pbca</i>	<i>P2₁/c</i>	<i>P</i>

Molecules of *m*-TPF4 also perfectly stack in columns, but with an important tilt into a chevron-like structure. The columns also lie in to parallel layers, separated by a substantial aliphatic sublayer from the chains in *meta* positions. Pairs of columns interact with F-F interactions (Figure 1, dotted green lines), and all columns are surrounded by the aliphatic chains. For both compounds, phase separation between chains aromatic cores and F-zones are optimized. Molecules of *p*-TP4 (Figure S48), arranged in triclinic lattice, do not form columns, in agreement with the absence of mesomorphism, with distances between centres of mass of ca. 3.66 Å. The comparison of *p*-TPF4 and *p*-TP4 shows that the presence of fluorine atoms strengthens the electrostatic interactions between molecules, making it easier to stack into columns. It can also be deduced that the molecular stacking of *p*-TPF4 is tighter than that of *m*-TPF4 as shorter intermolecular distances, thus stronger intermolecular forces, were found for the latter (3.3369 Å) than for the former (3.3584 Å). Of course, the

presence of these interactions and of the columns in the crystalline state in no way implies that they will be maintained in the mesophase, but if they do, they should likely contribute to the emergence of columnar mesomorphism.

Mesomorphism

The thermal stability of these compounds was first investigated by thermogravimetric analysis (TGA, Figure S49, Table S13) in dynamic mode (scan rate of 10 °C/min, under nitrogen). The results show that they all have very good thermal stability, with decomposition temperatures, determined at 5 % weight loss, around 300 °C, with no effect of the chain positional isomerism and chain-length. The thermal behaviour and thermotropic liquid crystalline properties of the synthesized molecules were studied by polarizing optical microscopy (POM, Figures 2 and S51-52), differential scanning calorimetry (DSC, Figures 3 and S50, Table S14), and small- and wide-angle X-ray scattering (S/WAXS, Figures 4 and S53-58, Tables 2 and S15).

Most of the fluorinated compounds were found to display fluid and highly birefringent optical textures, characteristic of columnar mesophases, with the presence of optically extinct zones between large growing focal conic domains (Figure 2). Within the *p*-TPF*n* series, only *p*-TPF4 is mesomorphic, whereas *p*-TPF6, the longer-chain homolog and *p*-TP4, with no fluorine, both directly melt in the isotropic liquid, as confirmed by DSC. For the *m*-TPF*n* series, mesomorphism is more favoured, as mesophases are seen for all the terms of the series, *n*=4-10, even though, for *n*=10, the mesophase is monotropic (Figure 3). A clear change of the optical texture could be seen between *m*-TPF4 and *m*-TPF6 (Figures 2 and S52), very likely in accordance to a change of mesophase symmetry. As above too, the non-fluorinated compound, *m*-TP4, is not mesomorphic.

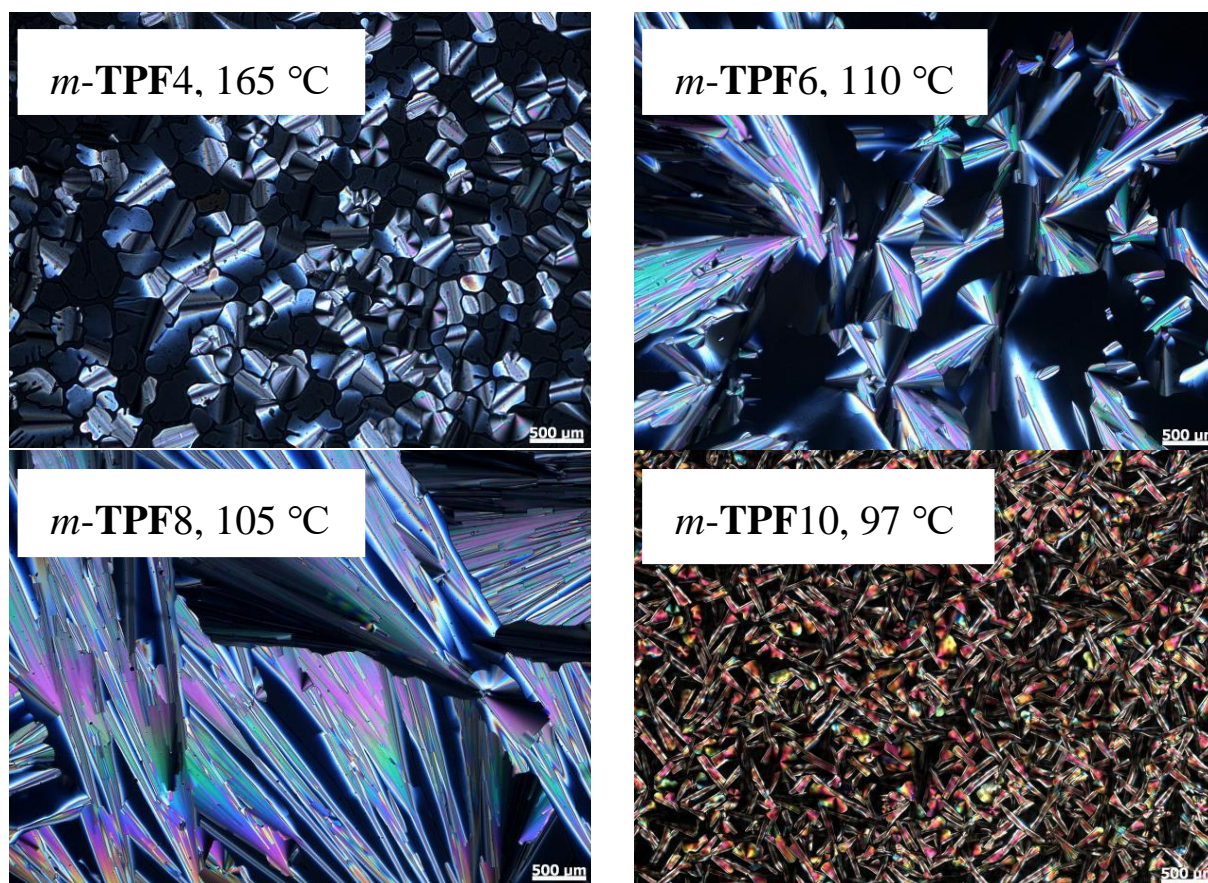


Figure 2. Representative POM textures of the terms of the *m*-TPF*n* series at different temperatures as a function of chain-length (recorded on cooling from the isotropic liquid).

From previous reports,^[34-36] this mesogenic platform bearing 4 identical peripheral chains, abbreviated as *mF*-TP*n*, was found to be influenced by the number of fluorine atoms (*m*) and by the length of the four alkoxy chains (*n*). Quite remarkably though, the short homologous compounds of the 4*F*-TP*n* series, with *n*=1 and 2, also exhibit a Col_{hex} mesophase up to ca 300 °C, but as chain-length increases (*n*>6), mesomorphism was strongly destabilized, or totally suppressed with the reduction of fluorine atoms (*m*<3). The same tendency is

observed with these compounds i.e. decrease/suppression of the mesomorphic range as the chain-length increases and with the loss of fluorine atoms. Furthermore, a significant drop in the mesomorphism is also observed with the chains' substitution pattern, highlighting the important role of isomerism in the promotion/suppression of mesomorphism in this family of compounds.

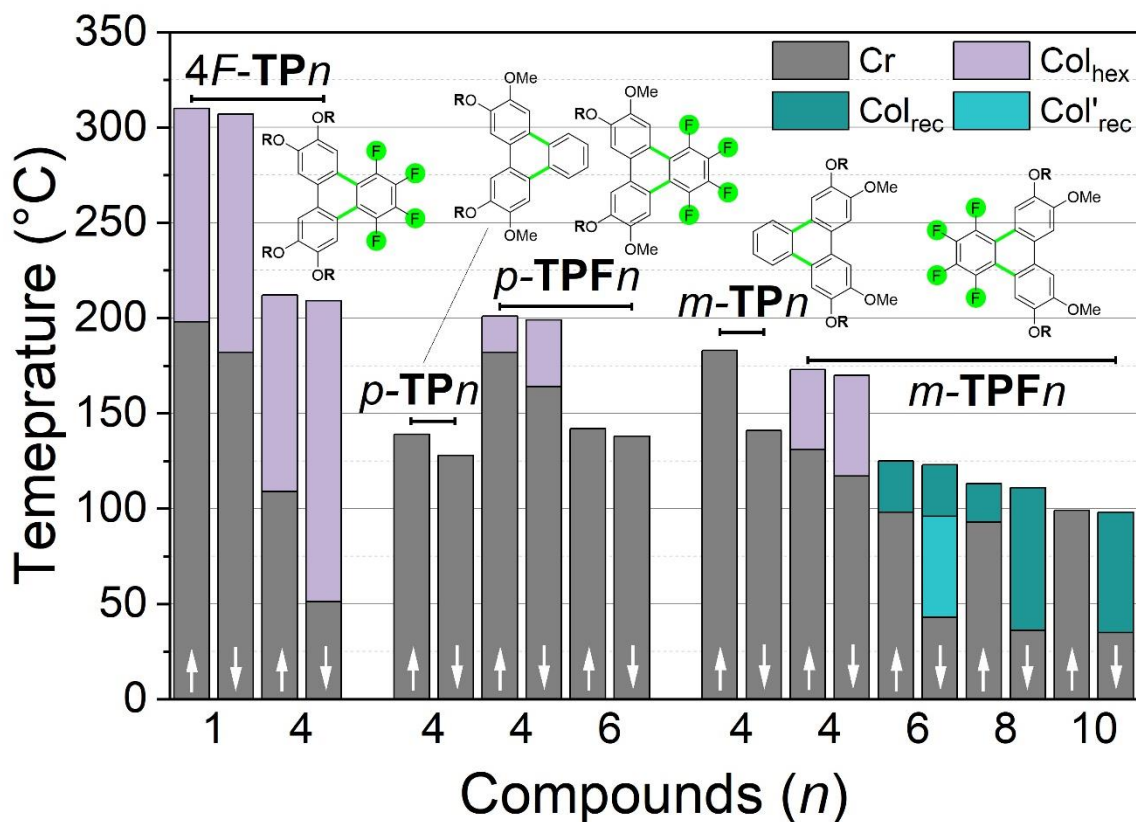


Figure 3. Phase diagram of *p*-TPF_{4/6}, *m*-TPF_{4/6/8/10}, *p*-TP₄, and *m*-TP₄ (compared with 4F-TP_{1/4}).^[34-36] White arrows indicate measurements performed on heating and cooling, respectively.

Temperature-dependent X-ray scattering experiments were systematically carried out on all compounds in order to unequivocally identify the nature of the mesophases. The X-ray patterns were recorded at several temperatures between room temperature and the isotropic liquid. Both *p*-TPF₄ and *m*-TPF₄ exhibit quasi identical X-ray patterns (Figure 4a), with only one sharp and intense small-angle diffraction peak, and, in the large-angle region, one weak broad scattering halo corresponding to the lateral distances between molten aliphatic tails (h_{ch}), and a very intense and sharp signal, corresponding to the π - π intracolumnar stacking interactions between adjacent aromatic cores. Although, due to the presence of only one sharp reflection, the mesophase attribution is not unequivocal (a square lattice could indeed be considered), but the textures observed by POM, as well as the mesomorphic behaviour of previously reported related 4F-TP_n compounds,^[34-37] the nature of the mesophases was logically attributed to Col_{hex}.

As mentioned above, the longer-chain homolog *p*-TPF₆ is not mesomorphous and melted directly in the isotropic liquid, and the compound crystallized on cooling (Figure S55), as confirmed by X-ray diffraction. The X-ray patterns exhibited by the longer-chain members of the *m*-TPF_n series ($n \geq 6$) were completely different (Figure 4b), corresponding to the formation of mesophases with another symmetry. In this case, a few sharp peaks could be observed in the small-angle range, that could only be indexed according to a rectangular symmetry, e.g. *p*2gg (Figures S56-58, Table S13). The wide-angle range was however similar to that of the compounds just described above with the presence of a very sharp and intense peak corresponding to π - π stacking, and still a weak broad and diffuse halo, corresponding to the molten chains, whose intensity increases with chain-length. Note that a transition between two phases of same symmetry (Col_{rec}-Col'_{rec}) was confirmed for *m*-TPF₆ by DSC and S/WAXS, though the low-temperature phase is monotropic.

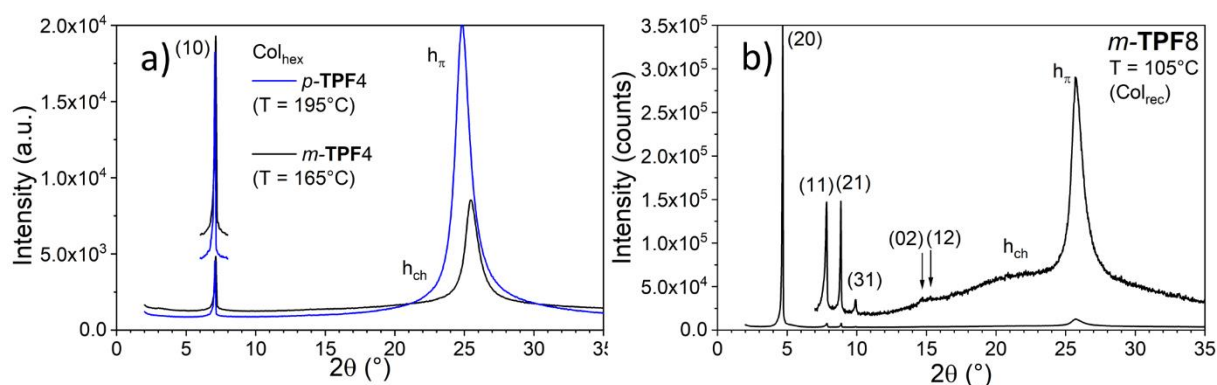


Figure 4. Representative S/WAXS patterns of *p*-TPF4 (a, Col_{hex}), *m*-TPF4/8 (a, Col_{hex}; b, Col_{rec}). Reflections at small angles have been enlarged for improving clarity.

Table 2. Mesophases' geometrical parameters.

Compound	Mesophase	Temperature ^[a]	a, b ^[b]	A (R) ^[b]	h_{π} (ξ) ^[c]	V_{mol} , ρ ^[a]	Z, h_{mol} ^[e]	ψ ^[f]	S ^[g]	q ^[g]
<i>p</i> -TPF4	Col _{hex}	195	14.64 -	185.65 -	3.57 (60)	697.5, 1.201	1, 3.76	18	-	-
<i>m</i> -TPF4	Col _{hex}	165	14.42 -	180.00 -	3.49 (56)	664.4, 1.261	1, 3.69	20	-	-
<i>m</i> -TPF6	LamCol _{rec}	118	33.68, 11.91	401.13 (2.83)	3.46 (67)	749.0, 1.243	2, 3.73	22	44.5	0.98
"	LamCol' _{rec}	90	33.40, 12.19	407.15 (2.74)	3.44 (81)	731.7, 1.272	2, 3.59	17	43.8	0.98
<i>m</i> -TPF8	LamCol _{rec}	105	37.98, 11.85	450.06 (3.20)	3.45 (67)	855.4, 1.197	2, 3.80	25	45.0	1.00
<i>m</i> -TPF10	LamCol _{rec}	90	40.70, 11.41	464.39 (3.57)	3.42 (66)	958.7, 1.165	2, 4.13	34	47.1	1.05

[a] Temperature of experiment (°C); [b] Lattice parameter, a and b (Å) and area, $A = a^2\sqrt{3}/2$ (Å²) for Col_{hex} and $a \times b$ for Col_{rec}; R, aspect ratio, $R = a/b$; [c] Average face-to-face stacking distance between consecutive mesogens, h_{π} (Å), determined from scattering maximum from SWAXS pattern, and ξ , correlation length (Å) calculated by Debye-Scherrer formula; [d] Molecular volume (Å³) and density (g cm⁻³) calculated from partial volumes of reference substances: $V_{\text{mol}} = V_{\text{ar}} + V_{\text{ch}}$, the sum of the volume of the aromatic part, V_{ar} (from reference compounds) and the volume of the chains, V_{ch} ; [e] $\rho = MW/(N_A \cdot V_{\text{mol}})$; [f] Z, number of columns per lattice, and h_{mol} , columnar slice thickness, $h_{\text{mol}} = Z \times V_{\text{mol}}/A$ (Å); [g] Out-of-plane tilt angle of mesogen cores inside columns (°), $\psi = \arcsin(h_{\pi}/h_{\text{mol}})$; [h] Chain cross-section area, $S = V_{\text{mol}}/d = b \times h_{\text{mol}}$, with d lamellar periodicity, and $d = a/2$; [i] q, packing coefficient, $q = S/2\sigma_{\text{ch}}$.

The hexagonal columnar phase of *p/m*-TPF4 thus emerges from the long-range quasi-antiparallel face-to-face stacking of the central rigid discoidal molecular parts into column, the columns being located at the nodes of the hexagonal array. The high intensity of the signal corresponding to the stacking periodicity (correlation length of columnar stacks of ca. 14-16 molecules) suggests that the flat mesogens pile up rather parallel to each other in the columns with no or small tilt ($\psi \approx 20^\circ$, Table 2). Such a small tilt angle allows free rotation between molecules within the columns, whilst optimizing arene-fluoroarene intermolecular interactions, leading to an average circular cross-section, thus to the Col_{hex} (Figure 5). Consequently, chains radiate around the columns homogeneously to form an infinite continuum between the rigid columns. The apparent deficit of chains is likely compensated by the chains from the surrounding neighbouring columns and from the free orientation of the molecules within the hexagonal plane. At short chain-lengths, therefore chain position isomerism does not affect this arrangement, and differences between *para*- or *meta*-chain' anchoring

positions are erased in the liquid crystalline phase, unlike in the crystalline state.

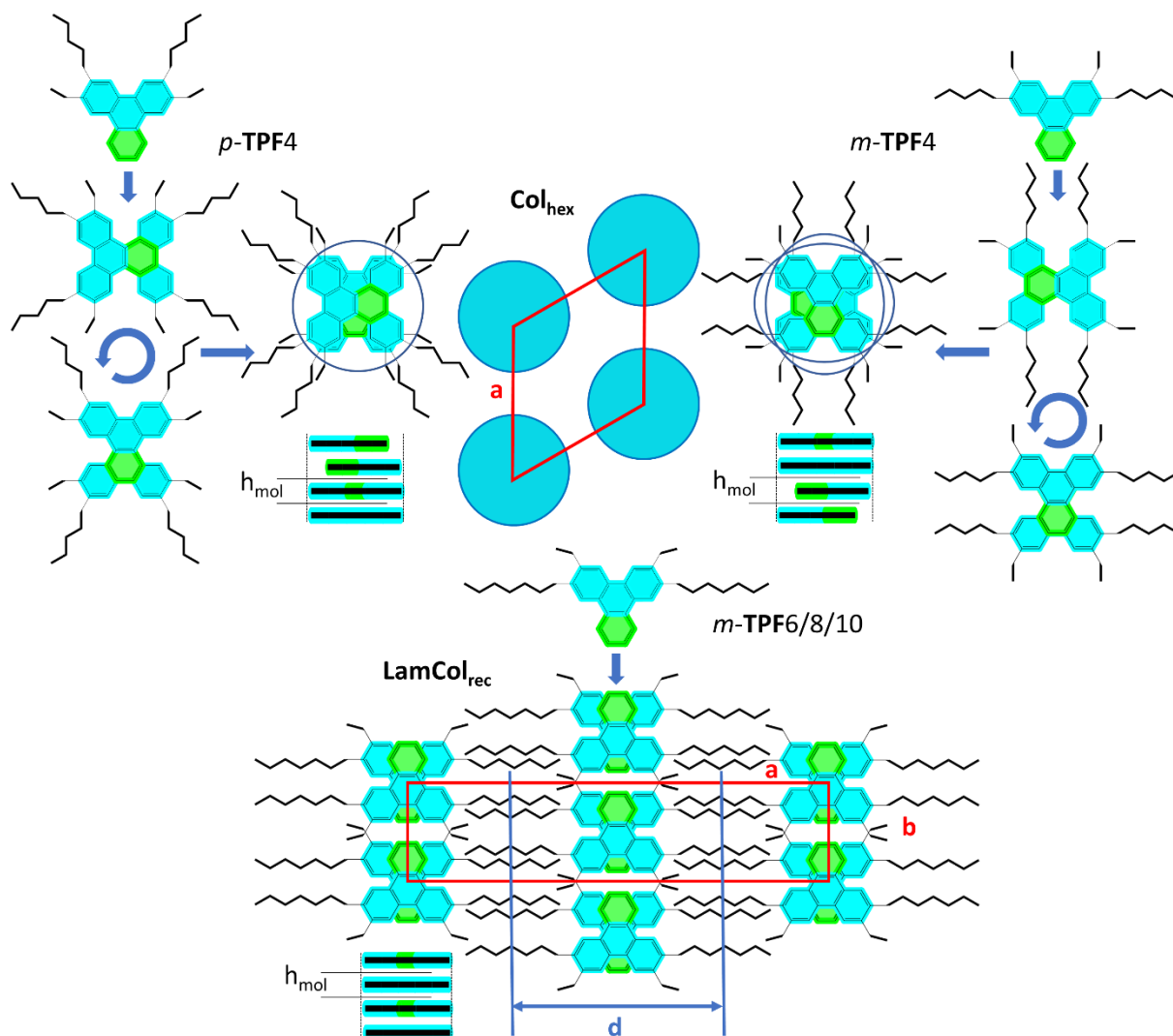


Figure 5. Schematic representation of the supramolecular assembly and organization in Col_{hex} and $LamCol_{rec}$ mesophases of the fluorinated compounds (the columns direction is perpendicular to the lattice plane). Columnar stacking in Janus compounds is driven by arene-perfluoroarene overlaps. Self-assembling into Col_{hex} or $LamCol_{rec}$ is driven by chain length and substitution pattern. See main text and Table 2 for abbreviations.

However, chains differentiation prevails when chains length increases. For the *para* system, mesomorphism simply vanishes for the longer chains homolog (p -TPF6). It should be recalled that for $4F$ -TP n molecules, mesomorphism was also found to decrease with chain lengthening, but this occurred at a later stage.^[34,36] In contrast, all *meta* compounds are mesomorphous, but they self-assemble in a different mesophase. As do their shorter homologs, molecules still stack to form columns, but due to the *meta*-anchoring of the chains to the triphenylene platform, the chains prefer now to radiate perpendicular to the molecular symmetry axis (C_{2v} axis), and perpendicular to the columnar axis, freezing the free rotation of the molecules. A better compromise to partition the space seems to be found via the regular alternation of aliphatic zones and aromatic parts into parallel rows. Thus, the columns lie into layers, alternating with aliphatic sublayers, but still preserving registry between the rows of columns with a $b/2$ shift at each alternation due to the compensation of the chains. Within the layers, the columns are close to each other, almost touching as only separated by the methylene groups (Figure 5). This lamellar arrangement is supported by the lateral chain cross-section area along the normal to the layer which equals that of two aliphatic chains (for one molecule) and with a chain packing coefficient almost equal to unity (Table 2). As such, the rectangular phase can be considered a lamello-columnar phase, $LamCol_{rec}$, with the columns in register from layer to layer, with a periodicity $d=a/2$. Possible representations of these supramolecular organizations and the self-assembly

mechanisms are displayed in Figure 5.

Photophysical properties

The photophysical properties of target molecules, *p*-TPF4 and *m*-TPF4, and of the non-fluorinated homologs, *p*-TP4 and *m*-TP4, were investigated. UV-Vis absorption, fluorescence emission and absolute fluorescence quantum yields were measured in dichloromethane (10^{-5} mol L⁻¹), and the results are summarized in Figure 6 and Table 3.

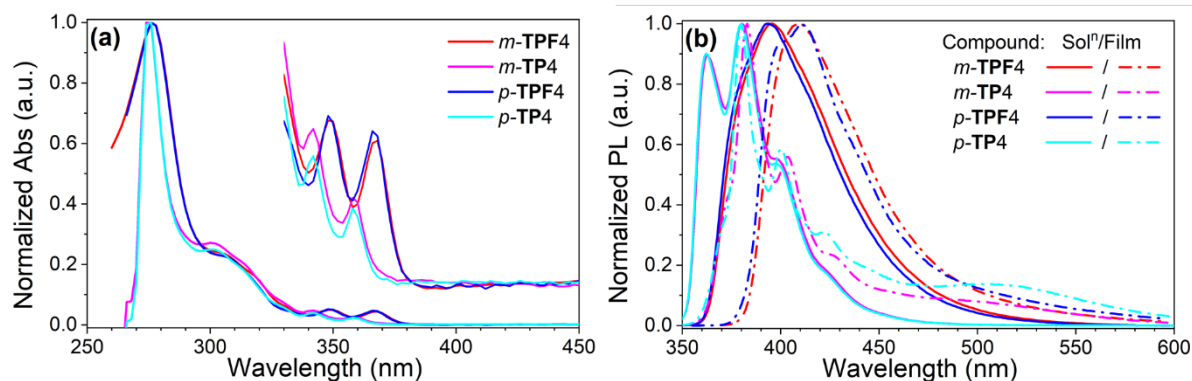


Figure 6. UV-vis absorption spectra (a), fluorescence emission spectra and thin film fluorescence emission spectra (b) of *p*-TPF4, *m*-TPF4, *p*-TP4 and *m*-TP4 in methylene chloride.

Table 3. Photophysical parameters of *p*-TPF4, *m*-TPF4, *p*-TP4 and *m*-TP4 in methylene chloride.

Cpds	$\lambda_{\text{abs}}^{[a]}$	$\epsilon (\times 10^4)^{[b]}$	$\lambda_{\text{em}}^{[c]}$	QY ^[d]	$\lambda_{\text{em}}^{[e]}$
<i>p</i> -TPF4	274	37.22	393	45.77	411
	351	1.84			
	366	1.74			
<i>m</i> -TPF4	276	32.00	395	41.36	409
	351	1.54			
	368	1.36			
<i>p</i> -TP4	276	7.41	380	12.12	380
	300	1.85			
	342	0.29			
	358	0.18			
<i>m</i> -TP4	274	7.92	380	10.61	383
	300	2.15			
	342	0.37			
	358	0.21			

[a] Position of maximum absorption peak, λ_{abs} (nm); [b] ϵ , Molar absorption coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$); [c,e] λ_{em} , fluorescence emission peak maximum in solution [c] and thin films [e] (nm); [d] QY, Fluorescence quantum yield (%).

UV-vis absorption spectra *p*-TPF4 and *m*-TPF4 are perfectly superimposable, and both show three distinct absorption peak maxima, of which a strong absorption near 276 nm, which may belong to the characteristic absorption band of the benzene ring, and two weaker absorption bands near 350 nm and 366 nm, which are attributed to the $\pi-\pi^*$ transition and to the intramolecular charge transfer (ICT) absorption band caused by fluorine atoms, all with molar extinction coefficients greater than 10^4 L mol⁻¹ cm⁻¹. Both *p*-TP4 and *m*-TP4 also are superimposable and present similar spectra to their fluorinated homologs, but in addition, they also have a weak absorption peak at 300 nm. As previously observed for related compounds,^[35] the fluorination of the aromatic ring produces a small redshift of the absorption maxima. Clearly too, the relative position of the alkoxy chain have no effect on the absorption properties. Fluorescence emission spectroscopy shows that *p*-TPF4 and *m*-TPF4 have strong fluorescence emission, centred at around 395 nm, and the quantum yields in dichloromethane solution were found to be ca. 46 % and 41 %, respectively, which may result from the π -conjugated structure of TP molecules.^[35] The fluorescence spectra of the non-fluorinated homologs *p*-TP4 and *m*-TP4 (in dichloromethane, at 10^{-5} mol L⁻¹) are more structured, with maxima at lower wavelengths than

the fluorinated homologs, and the quantum yields are also much smaller, ca.12 % and 11 %, respectively, which shows that the π -electrons of fluorine atoms compared with hydrogen atoms expand the degree of conjugation of the molecules. Fluorescence spectra in thin films are similar to solution's, but maxima are slightly shifted for *p*-TPF4 and *m*-TPF4, whereas those of *p*-TP4 and *m*-TP4 are almost superimposable. The maximum emission wavelength of *p*-TPF4 and *m*-TPF4 in solution and the fluorescence spectra of the thin film are therefore redshifted with respect to the non-fluorinated homologs, which may be that the fluorine-containing molecules are flatter, and according to the results of single crystal structures, the fluorine atoms would favour closer separation between molecules and thus intermolecular interactions are stronger. In summary, the position of the alkoxy chains has no effect on the photophysical properties of this series of compounds, whilst the influence of fluorine atoms is more obvious. Both *p*-TPF n and *m*-TPF n have good luminous performance, and have potential application value in the field of photoelectric materials such as light-emitting diodes.

Conclusions

In this work, nucleophilic 2,2'-dilithium biphenylenes, generated in situ by the reaction of dibromobiphenyl with butyl lithium, reacted with electrophilic perfluorobenzene by nucleophilic substitution S_NAr reaction, to yield *p*-TPF n and *m*-TPF n , respectively, which are π -conjugated disc-shaped liquid crystal compounds with good thermal stability. The chain substitution pattern was found to affect the self-assembly of the molecules in both crystalline and liquid crystalline states, a rather unexpected result for DLCs, and that *m*-TPF n are "better" mesogens than their *p*-TPF n homologs. The compounds show either liquid crystalline Col_{hex} or LamCol_{rec} mesophases, whose columnar structure cohesion is certainly enhanced by arene-perfluoroarene interactions between stacked molecules. They exhibit interesting emission properties in both solid and in solution, with absolute fluorescence quantum yields of up to 46 % measured in the solution, and emitting blue-violet light in both solution and thin films.

Such a synthetic methodology could be easily exploited further for the design of more complex PAH molecular structures (fluorinated and non-fluorinated) that could yield original supramolecular self-organizations and interesting optical and semiconducting properties for potential applications in liquid crystal displays and organic optoelectronic functional materials. Research in this area is currently underway.

Supporting Information

Experimental methods and instrumentation, synthesis and characterization, ¹H, ¹³C and ¹⁹F NMR (Figures S1-34), HRMS (Figures S35-42), EA, Single crystal X-ray structures (Figures S43-48, Tables S1-12), TGA (Figure S49, Table S13), DSC (Figure S50, Table S14), POM (Figures S51-52), S/WAXS (Figures S53-58, Table S15) are given in the supporting information. authors have cited additional references within the Supporting Information.

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Conflicts of interest The authors declare no conflict of interest.

Data Availability Statement The data that support the findings of this study are available in the supplementary material of this article.

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