ARTICLE

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Synthesis, optical properties, crystal structures and phase behaviour of selectively fluorinated 1,4-bis(4′-pyridylethynyl)benzenes, 4-(phenylethynyl)pyridines and 9,10-bis(4′-pyridylethynyl)-anthracene, and a $Zn(NO_3)_2$ coordination polymer

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A series of selectively fluorinated and non-fluorinated rigid rods based on the 4-pyridylethynyl group, namely 1,4-bis(4′-pyridylethynyl)benzene (**1a**), 1,4-bis(4′-pyridylethynyl)tetrafluorobenzene (**1b**), 1,4-bis(2′,3′,5′,6′-tetrafluoropyridylethynyl)benzene (**1c**), 1,4-bis(2′,3′,5′,6′-tetrafluoropyridylethynyl)tetrafluorobenzene (**1d**), 9,10-bis(4′-pyridylethynyl)anthracene (**2**), 4-(pentafluorophenylethynyl)pyridine (**3a**) and 4-(phenylethynyl)-tetrafluoropyridine (**3b**) were prepared in good yields using Pd/Cu-catalysed Sonogashira cross-coupling reactions and/or lithium chemistry involving nucleophilic aromatic substitution. UV-Vis absorption and fluorescence spectra for **1a–d** and **2** are reported. The X-ray crystal structures of **1b**, **1c**, **2**, **3a** and **3b** show a variety of packing motifs, none of which involve arene–perfluoroarene stacking. The phase behaviour of **1a–1c** has been studied by differential thermal analysis and transmitted polarised light microscopy. Compound **1b** exhibits an ordered phase between 227.6 and 272.5 °C which is either hexatic B or crystal B. A 1 : 1 complex (**4**) between **1b** and $Zn(NO_3)_2$ has been prepared; its crystal structure consists of zig-zag polymer chains held together by hydrogen bonds.

Introduction

There has been intense activity in the area of supramolecular self-assembly within the last decade.[1] Metal–ligand coordination has proved useful in the assembly of functional molecular materials[2] which include a variety of one-dimensional chains, two-dimensional sheets and three-dimensional networks containing cavities of various sizes.[3] The goal is the design and assembly of structures with potential applications as catalytic, luminescent, and magnetic materials, and porous structures for use in separations.[4]

N,*N*′-Bridging ligands built from two 4-pyridyl units have been widely utilised in the construction of these structures.[5] Although 4,4′-bipyridyl has been employed extensively as a bridging ligand in networks with a high degree of porosity,[6] several groups have reported the use of longer bis(4-pyridyl) units of the type Py–X–Py (Py = 4-pyridyl; X = CH_2CH_2, CH=CH, C≡C, C≡C–C≡C, C_6H_4, $C_{14}H_8$, C_6F_4, C≡C–C_6H_4–C≡C) as ligands.[7] Fujita recently reported the use of a longer bis(4′-pyridyl)-*p*-*p*-*p*-triphenylene ligand in the construction of a 24 × 24 Å square ladder.[8]

The nature of the bridging ligand plays an important role in manipulating the overall structure of the coordination network and in the recognition ability of a system, which depends on the nature of the cavity. Fluorination of the aromatic ligand can lead to specific recognition of electron-rich arene compounds, and can favour clathrate formation over interpenetration.[9]

This prompted us to synthesise a series of fluorinated (4-pyridylethynyl)benzene-based rigid rods for use in self-assembly. Several *ortho*-ethynyl-substituted fluorinated pyridine derivatives have been prepared previously.[10] In this paper, we report the synthesis of a series of fluorinated 1,4-bis(4′-pyridylethynyl)benzenes, 1,4-bis(4′-pyridylethynyl)anthracene, and 4-(pentafluorophenylethynyl)pyridine by Sonogashira cross-coupling. We also report the synthesis of 4-(phenylethynyl)tetrafluoropyridine *via* nucleophilic substitution on pentafluoropyridine by lithium phenylacetylide, and the preparation and crystal structure of a 1 : 1 coordination polymer of 1,4-bis(4′-pyridylethynyl)tetrafluorobenzene with zinc(II) nitrate.

Results and discussion

Synthesis

Most of these compounds were prepared using the Sonogashira Pd/Cu-catalysed cross-coupling reaction, an efficient method of synthesizing aryl and heteroaryl alkynes in good yields *via* the

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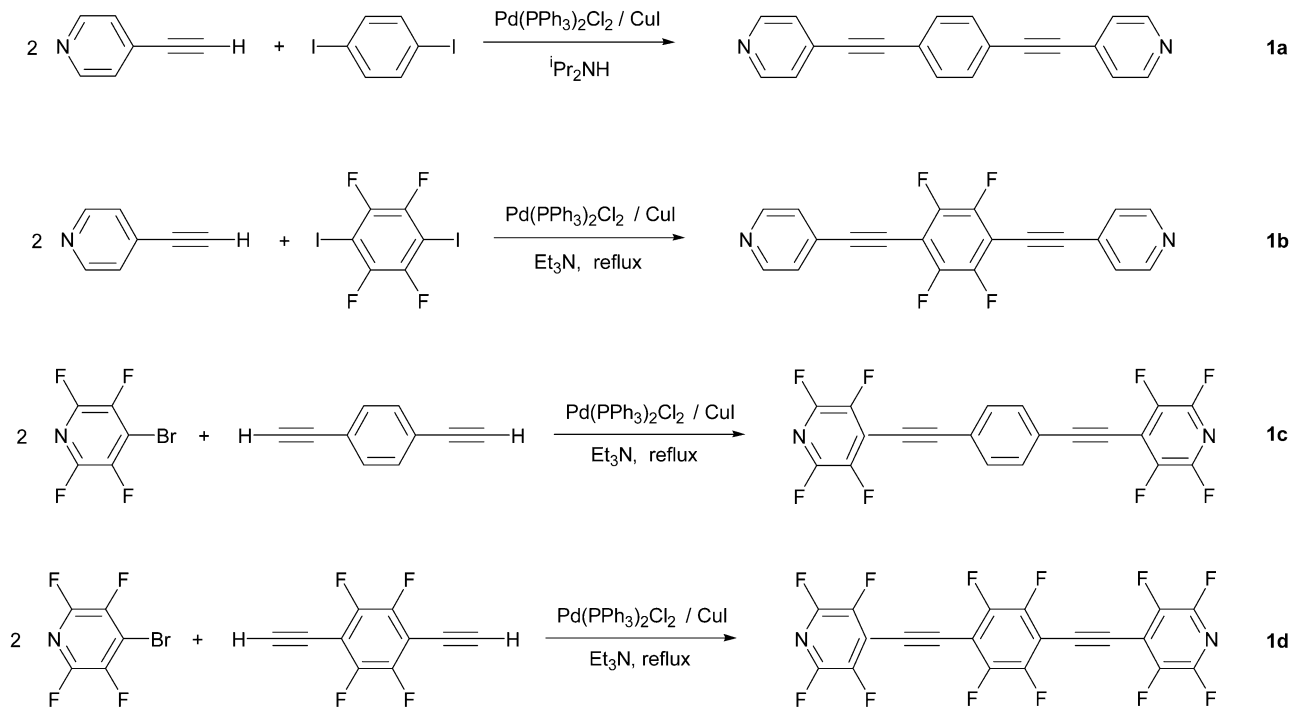
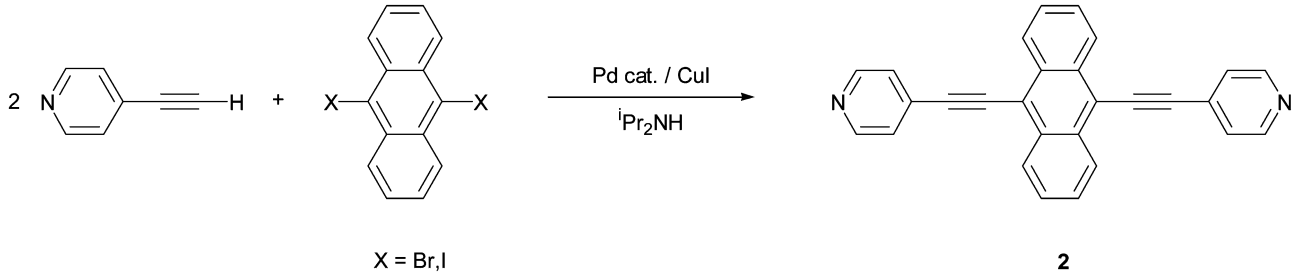


Scheme 1 Synthesis of 1,4-bis(4′-pyridylethynyl)benzenes (**1a–d**).

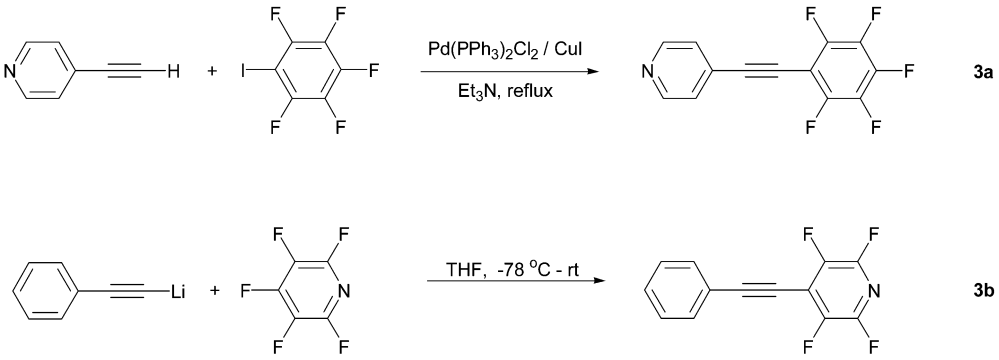
coupling of aryl halides with terminal alkynes, with aryl iodides being more reactive than corresponding bromides.[11] Two compounds were synthesised by nucleophilic aromatic substitution by lithium acetylides on pentafluoropyridine. Similar substitution reactions on highly fluorinated arenes have been reported.[12]

The synthesis of the 1,4-bis(4′-pyridylethynyl)benzenes (**1a–d**) is shown in Scheme 1. Compounds **1a** and **1b** contain unfluorinated pyridyl rings and were prepared by coupling two equivalents of 4-ethynylpyridine with 1,4-diiodobenzene and 1,4-diiodotetrafluorobenzene respectively. The coupling to form **1a** occurred in two hours at room temperature in diisopropylamine; however, **1b** required four hours reflux in triethylamine. In contrast, compounds **1c** and **1d** containing fluorinated pyridyl rings were prepared *via* the coupling of two equivalents of 4-bromotetrafluoropyridine with 1,4-diethynylbenzene or 1,4-diethynyltetrafluorobenzene, respectively in refluxing triethylamine. We, and subsequently several other groups,[13] have reported the synthesis of the parent compound **1a** as a yellow–orange powder with yields ranging from 15 to 99%. In the present study, **1a** was obtained in 60% yield as a white powder after column chromatography on basic alumina using hot toluene as the eluent. Thus, it seems likely that the yellow–orange colour observed previously was due either to a trace impurity or to the presence of a coloured polymorph. Compounds **1b** and **1c** were worked-up analogously in comparable yields. We have also prepared compound **1c**, although in much lower yield, from the di-lithiation of 1,4-diethynylbenzene followed by quenching with two equivalents of pentafluoropyridine. Compound **1d** could only be isolated in 20% yield from Sonogashira reactions, and was shown by EI mass spectrometry to contain traces of the butadiyne derivative $C_5F_4N–C{\equiv}C–C_6F_4–C{\equiv}C–C{\equiv}C–C_6F_4–C{\equiv}C–C_5F_4N$, which have been shown[13a] to result from hydrodehalogenation pathways during Sonogashira reactions with highly fluorinated systems, as well as an unidentified species with a peak at $m/e = 530$.

The synthesis of 9,10-bis(4′-pyridylethynyl)anthracene (**2**) *via* Sonogashira coupling is shown in Scheme 2. Two alternative syntheses were employed; in the first, two equivalents of 4-ethynylpyridine were coupled with 9,10-diiodoanthracene in diisopropylamine at room temperature, using the well-known catalyst precursor $Pd(PPh_3)_2Cl_2$. In the second method, 4-ethynylpyridine was coupled to the less reactive, but commercially available, 9,10-dibromoanthracene in triethylamine at room temperature, using a more active catalyst system prepared *in situ* from $Pd(PhCN)_2Cl_2 + 2P^tBu_3$.[14] Column chromatography on basic alumina using hexane/ethyl acetate afforded the desired compound which was judged pure by NMR spectroscopy and EI MS. However, in spite of repeated attempts, on a variety of samples, a satisfactory elemental analysis could not be obtained. As the analyses were always rather low in carbon, it appears that this may be the result of incomplete combustion.



Scheme 2 Synthesis of 9,10-bis(4′-pyridylethynyl)anthracene (**2**) (for X = I, Pd cat. = $Pd(PPh_3)_2Cl_2$; for X = Br, Pd cat. = $Pd(PhCN)_2Cl_2$/2 P^tBu_3).



Scheme 3 Synthesis of (4-pyridylethynyl)benzenes (**3a–b**).

The compound 4-(pentafluorophenylethynyl)pyridine (**3a**) was obtained in moderate yield *via* the coupling of one equivalent of 4-ethynylpyridine with iodopentafluorobenzene in refluxing triethylamine. In contrast, 4-(phenylethynyl)tetrafluoropyridine (**3b**) was synthesised in high yield *via* aromatic nucleophilic substitution of pentafluoropyridine by lithium phenylacetylide at −78 °C in dry THF, with substitution taking place exclusively at the *para*-position.[12] Column chromatography on silica, eluting with hexane, gave a high yield of analytically pure product. This compound has been reported previously from the reaction of trimethylsilylethynylbenzene with pentafluoropyridine in the presence of KF in DMF at room temperature.[15] These reactions are shown in Scheme 3.

Careful layering of an ethanol solution of $Zn(NO_3)_2{\cdot}6H_2O$ over a CH_2Cl_2 solution of **1b** led to the deposition of a fine precipitate and the slow growth, at the layer interface, of light-yellow crystals of the coordination polymer, **4**. Polymer **4** contains no water, as the Zn(II) coordination environment is essentially tetrahedral, with two bound pyridyl nitrogens and two monodentate NO_3 ligands, *vide infra*.

Luminescence

As these compounds are analogues of 1,4-bis(phenylethynyl)-benzenes[13a] and 9,10-bis(phenylethynyl)anthracenes[11c] which are highly luminescent, we investigated their UV-vis absorption and emission spectra, which are summarised in Table 1. The bis(4-ethynylpyridyl)benzene compounds **1a–d** all absorb in the region 314–320 nm with the extinction coefficient increasing as the degree of fluorination increases. Fluorination of the compounds leads to the presence of a shoulder near 333 nm in compounds **1b** and **1c**, but a distinct sharp peak at 336 nm was observed in the fully fluorinated compound **1d**, which, in the latter case, could be a result of impurities (*vide supra*). There is a larger variation in their emission maxima with fluorination, compared to their absorption spectra. Expectedly, compound **2** absorbs at a longer wavelength of 436 nm as a result of increased conjugation in the anthracene. This compound is highly emissive, at 574 nm, which makes it suitable for use as a fluorescent chromophore.

Protonation of the compounds in solution by addition of trifluoroacetic acid results in a bathochromic shift in the UV-vis absorption and emission spectra of all of the compounds, the change in absorption wavelength being larger for the non-fluorinated compounds **1a** and **2**. The emission wavelength of **2** is red shifted from 574 to 634 nm and the solution changes colour from fluorescent green to orange.

Crystal structures

The molecular structures of **1b**, **1c**, **2**, **3a** and **3b**, determined by single-crystal X-ray diffraction, are shown in Fig. 1. Molecules **1b** and **1c** have crystallographic inversion centres, while **3a** and **3b** have no crystallographically imposed molecular symmetry. All four molecules adopt nearly planar conformations, with the dihedral angles τ between the benzene and the pyridine rings being 2.5, 5.6, 0.4 and 3.4°, respectively. Molecule **2** lies on a crystallographic twofold axis, passing through the atoms N(1), C(3), C(4), C(5), C(6), C(13), C(14), C(15), C(16) and N(2). The two pyridine rings of the molecule have different orientations, rotated by 5.0 and 64.8° with respect to the anthracene plane. As shown in Table 2, N–C bonds in fluorinated pyridine rings are significantly shortened, and the single C–C bonds between the acetylene and arene groups are marginally shorter when the latter is fluorinated. Both effects can be explained by the polarity of these bonds being diminished or reversed by the induction effect of fluorine substituents.

Complex **4** has a polymeric (*catena*) structure (Fig. 2). The zinc atom lies on a twofold axis and has a distorted tetrahedral N_2O_2 coordination with two **1b** ligands (whose planes are almost perpendicular) and two monodentate nitrate anions. Thus, the structure contains an infinite zig-zag chain –**1b**–Zn–**1b**–Zn–, running parallel to the [2 0 $\bar{1}$] direction. The bridging **1b** ligand has crystallographic inversion symmetry and a nearly planar conformation (τ = 6.1°). The changes in bond distances compared to those in the crystal structure of pure **1b** are within 3 e.s.d.'s, although they are not inconsistent with an increased conjugation along the rod. Similar polymeric structures have been found[16] in a series of (4,4′-bipyridine)ZnX_2 complexes, where X = $S_2COCH_2CHMe_2$,[16a] SPh,[16b] $SP(OPr^i)_2S$,[16c] salicylate,[16d] or SCOPh.[16e]

Crystal packing of the compounds is basically of two different modes. The structure of **1b** is composed of flat layers of molecules (Fig. 3), approximately parallel to the lattice plane (1 0 3). The long axes of molecules throughout the structure form two parallel sets with an 81° angle between them. Of the

Table 1 Absorption and luminescence data in acetonitrile

Compound	λ_{max}/nm	log ε	λ_{max} (emission)/nm	λ_{max}[a]/nm	λ_{max} (emission)[a]/nm
1a	315	3.33	402	366	424
1b	314	3.98	362	336	486
1c	320	4.33	446	338	473
1d[b]	316, 336(sh)	4.65			
2	436, 462	4.21, 4.24	574	510	634

[a] After addition of trifluoracetic acid. [b] The shoulder in the absorption spectrum *may* be due to impurities; the emission spectrum is not reported, as the impurities are likely to be highly luminescent; see text.

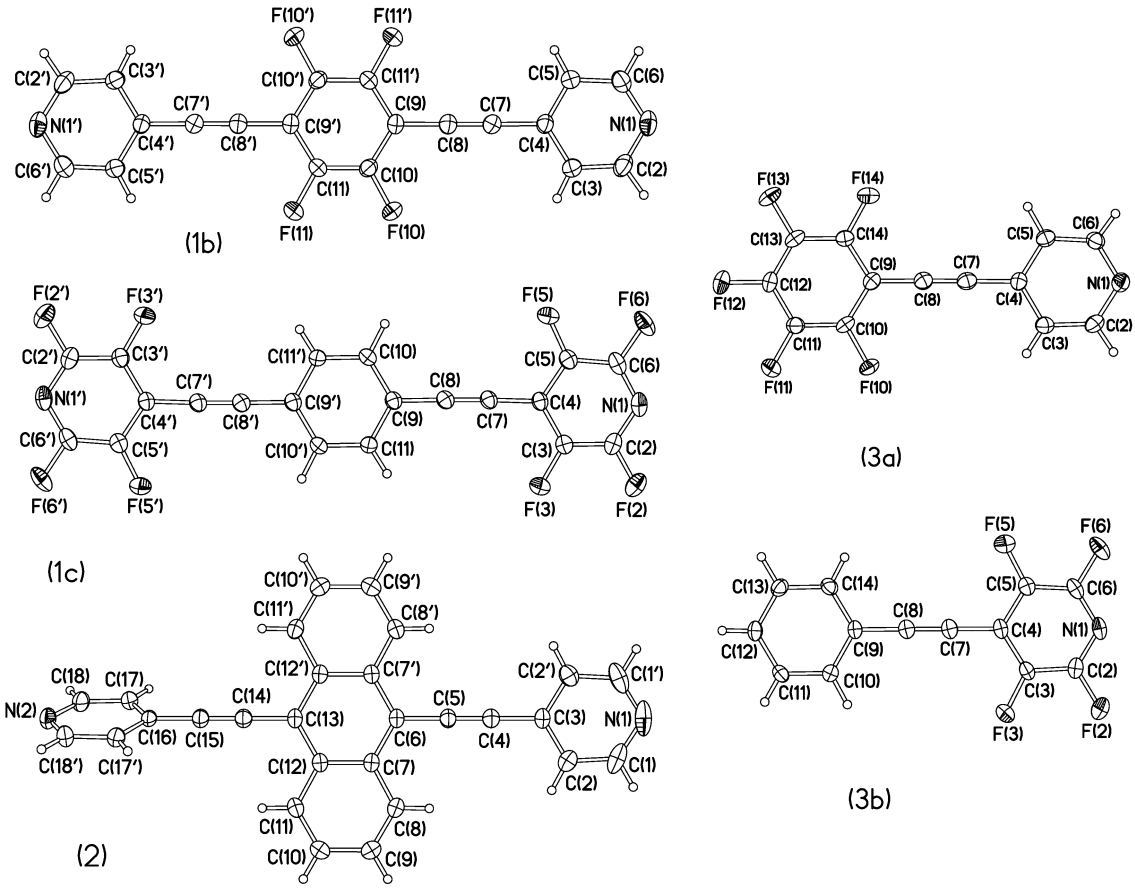
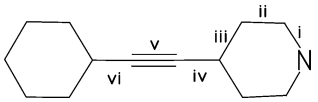


Fig. 1 Molecular structures of **1b**, **1c**, **2**, **3a** and **3b**, projected on the plane of the central rings and showing 50% displacement ellipsoids. Atoms generated by inversion centres (**1b**, **1c**) or twofold axis (**2**) are primed.

Table 2 Selected bond distances (average) in Å



Bond	1b	1c	2	3a	3b	4
i	1.338(2)	1.310(4)	1.332(2)	1.342(3)	1.305(2)	1.347(2)
ii	1.385(2)	1.381(4)	1.384(2)	1.374(3)	1.383(2)	1.380(2)
iii	1.395(2)	1.390(4)	1.394(1)	1.395(3)	1.393(2)	1.397(2)
iv	1.435(2)	1.423(3)	1.433(2)	1.427(3)	1.426(2)	1.427(2)
v	1.193(2)	1.199(4)	1.198(2)	1.199(3)	1.196(3)	1.199(2)
vi	1.424(2)	1.432(3)	1.430(2)	1.414(3)	1.438(2)	1.414(2)

four symmetry-independent H atoms, one is involved in a C(3)–H···N(1) hydrogen bond and the rest in H···F contacts with other molecules of the same layer. The H···N distance§ of 2.34 Å is significantly shorter than the sum of van der Waals radii of 2.74 Å, while H···F distances (2.51–2.52 Å) are close to the corresponding sum (2.56 Å).[17] Adjacent layers are offset to such an extent that there is practically no stacking interaction between aromatic rings. The shortest interlayer contact, between C(6) and C(11), is 3.35 Å.

A layered motif is also adopted by **3a**; in this triclinic structure, all molecules are mutually parallel/antiparallel (Fig. 3). The intermolecular but intra-layer contacts between hydrogens and negatively charged atoms are longer than in **1b**, but more numerous. Thus, H(1) and H(2) contact two F atoms each (H···F 2.61–2.69 Å), H(5) contacts one F and one N atoms at 2.60 and 2.45 Å respectively, while H(4) contacts one F atom at 2.48 Å. In its packing motif, and in the lattice parameters, **3a** can be described as a distorted (sheared) analogue of the structures of $C_6F_5C{\equiv}CPh$ or of the 1 : 1 complex between $PhC{\equiv}CPh$ and $C_6F_5C{\equiv}CC_6F_5$.[18a] The two latter structures are dominated by stacks of alternating phenyl and pentafluorophenyl rings, as are the structures of pentafluorostilbene,[18b] pentafluorodiphenylbutadiyne[18c] partially fluorinated bis(phenylethynyl)benzenes[18d,e] and other related systems.[18f–k] However, in **3a**, the offset is much larger, so that the Py and C_6F_5 rings overlap either by a single atom [C(5) eclipsed with C(9), at a 3.33 Å distance], or not at all.

In contrast, the structures of **1c** and **3b** are composed of infinite stacks of molecules (Fig. 4). Adjacent molecules in a stack are related by a translation (*b* in **1c**, *a* in **3b**) and are therefore strictly parallel but are offset in the direction of their long axes, so that both the benzene and the pyridine rings overlap with C≡C bonds (Fig. 5). The mean interplanar separations are 3.41 Å in **1c** and 3.35 Å in **3b**. The stacks are arranged in a γ, or flattened herringbone pattern,[19] so that the

§ An idealized C–H distance of 1.08 Å was used for all calculations of hydrogen contacts.

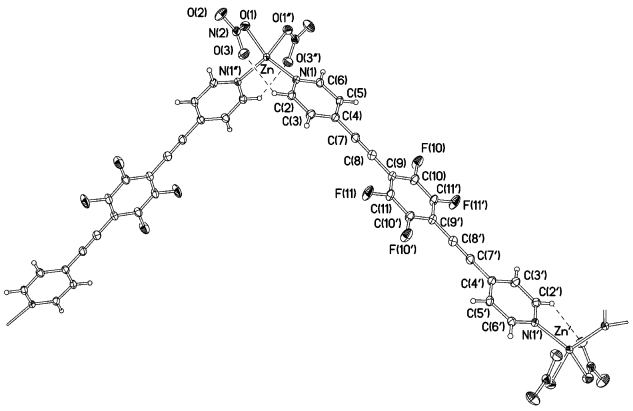


Fig. 2 Part of the polymeric structure **4**. Atoms generated by an inversion centre are primed, those generated by a twofold axis are double-primed. Important bond distances and angles within the organic ligand are provided in Table 2. Selected bond distances (Å) and angles (°) in the coordination sphere of Zn are: Zn–O(1) = 1.9918(13), Zn–N(1) = 2.0267(13), N(1)–O(1) = 1.296(2), N(1)–O(2) = 1.222(2), N(1)–O(3) = 1.242(2); O(1)–Zn–O(1′) = 88.24(8), N(1)–Zn–N(1′) = 109.19(8).

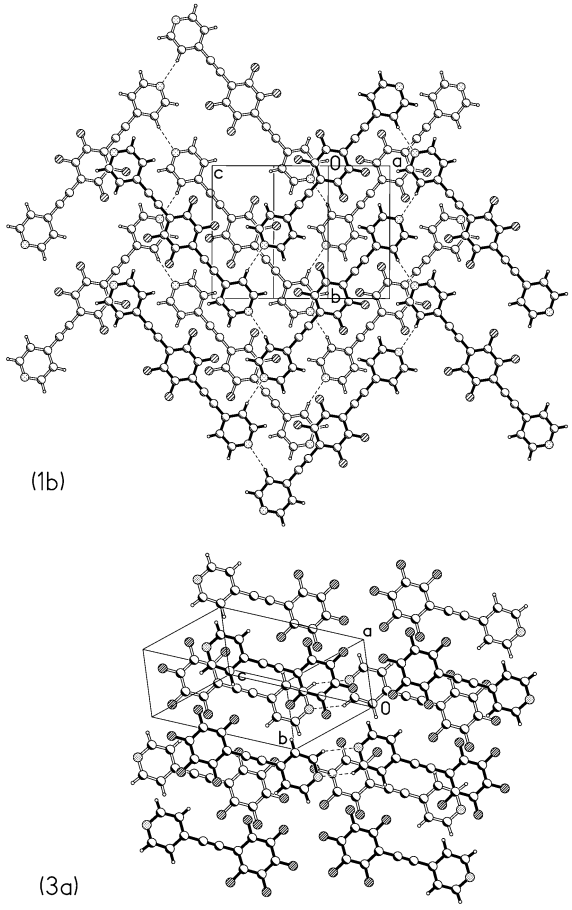


Fig. 3 Crystal packing of **1b** and **3a**, showing intermolecular hydrogen bonds C–H···N.

molecules in adjacent stacks form a dihedral angle of 84.5° (**1c**) and 84.6° (**3b**) and have a close contact through their N atoms, forming a zig-zag N···N···N chain (N···N 3.21 Å in **1c**, 3.24 Å in **3b**). In the structure of **1c**, the stacks form a continuous herringbone layer; in **3b** there are only two-stack herringbone arrays, with the "arrows" directed in both *a* and $-a$ directions, as well as those differing by a 90° pseudo-rotation around this axis (Fig. 4). The two independent H atoms in the structure **1c** form two H···F contacts each (2.55–2.74 Å), whilst in **3b** four H atoms form one to three contacts each (2.56–2.79 Å) and the

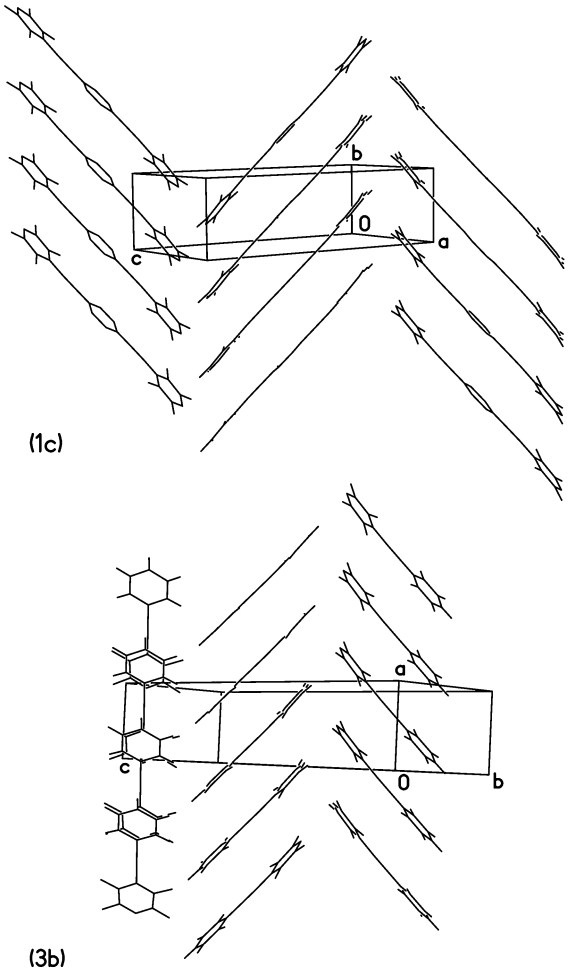


Fig. 4 Crystal packing of **1c** and **3b** (H atoms are omitted for clarity).

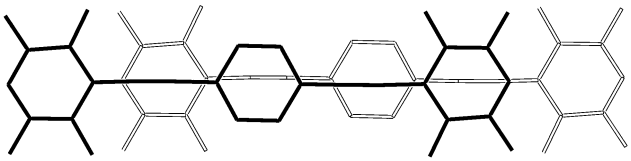


Fig. 5 Overlap of adjacent molecules in a stack of **1c**.

fifth H atom forms none. In both structures these contacts are slightly longer than in **1b**, and N···H contacts are rendered impossible.

In the structure of **2**, the nearly-planar parts of the molecules are stacked in a head-to-tail fashion, so that the anthracene moiety overlaps with the almost parallel pyridine ring while the rotated pyridine rings lie between the stacks. The mean interplanar separation in a stack is 3.40 Å and the shortest intermolecular contact C(3)···C(7) is 3.41 Å. As in the crystal structures of **1c** and **3b**, the pyridine nitrogen atoms of **2** do not accept any hydrogen bonds.

The packing motif of **4** can be described as a layer of zig-zag chains (related by the *b* translation), followed by an antiparallel layer (Figs. 6 and 7). The apparent resemblance to the packing motif of **1c**, however, is deceptive; adjacent **1b**-ligands in **4** have a large lateral offset and no overlap between the rings, rather like in the structures of **1b** and **3a**. Of the four independent H atoms, one is engaged in a relatively strong intra-chain hydrogen bond C(2)–H···O(3) (H···O 2.30 Å, *cf.* the sum of van der Waals radii[17] of 2.68 Å) and the rest in inter-chain interactions, two with O atoms (H···O 2.39 and 2.45 Å) and one with F (H···F 2.41 Å).

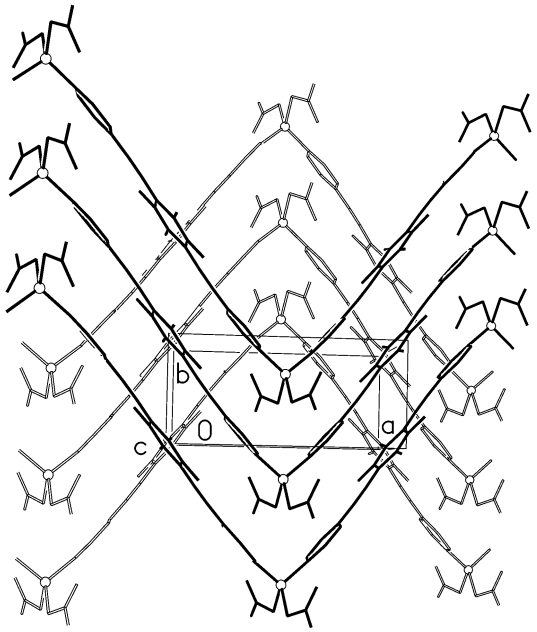


Fig. 6 Crystal packing of **4** (H atoms are omitted).

Thus, neither phenyl and tetrafluoropyridyl, nor pyridyl and pentafluorophenyl moieties form the mixed-stack motif, which is typical for arene–perfluoroarene complexes[20] and is also observed in the structures of the related compounds 4-biphenyl-tetrafluoropyridine, 2,4,6-trimethylphenylazo-tetrafluoropyridine and 2,4,6-trimethylphenylazoxytetrafluoro-pyridine.[21]

Phase behaviour

In a melting point capillary, in air, only **1a** showed a clean melting point of 192–193 °C. Slow heating of the other compounds led to decomposition as indicated in Table 3. Given the rigid-rod shape of these systems, the phase behaviour of compounds **1a**, **1b** and **1c** was studied in more detail using differential thermal analysis (dta) and transmitted polarised light microscopy (tplm). The phase transition data are also given in Table 3. Only **1b** was found to exhibit mesomorphic behaviour. Thus, a mesophase appeared at 227.6 °C (estimated from tplm) upon heating, which persisted until the sample degraded at 273.5 °C. The optical texture of this phase as observed by tplm, and shown in Fig. 8, is consistent with either hexatic B or crystal B. Whilst distortion under stress points to crystal B, rounded edges of the domains are suggestive of the possibility of the more fluid hexatic B phase. A definitive assignment of the phase requires X-ray diffraction studies at high temperature, perhaps in the presence of an aligning magnetic field, and such experiments are planned. Suffice it to say at this time that a new hexagonal phase is observed at higher temperatures which is clearly distinct from the one in the single-crystal X-ray structure.

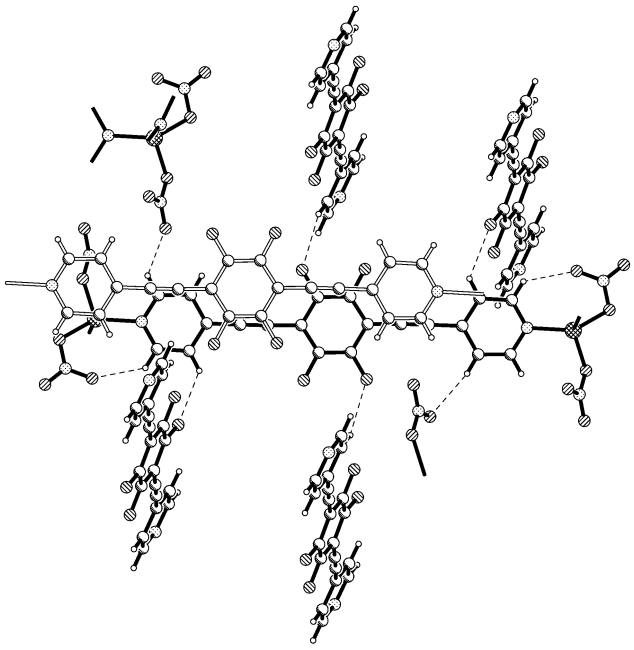


Fig. 7 Overlap of adjacent molecules in a stack of **4**, also showing the hydrogen bonding between the stacks.

Table 3 Phase behaviour data for compounds **1a–d** and **2**

Compound	Mp[a]/°C	Transitions upon heating[b]
1a	192–193	K 192.3 I
1b	235[dec]	K 227.6 hexatic B/crystal B 272.5 deg[c]
1c	247[dec]	K 313.9 I/deg
1d	166[dec]	N/A
2	233[dec]	N/A

[a] Meltemp II apparatus, uncorrected; [dec] = decomposition noted on slow heating. [b] From DTA experiments. [c] Transition temperatures from tplm; see text.

Conclusion

Sonogashira palladium/copper-catalysed cross-coupling reactions provide a practical synthetic route to several selectively fluorinated rigid rods containing the 4-pyridylethynyl group, whereas others were prepared *via* lithium chemistry. These compounds are highly luminescent. Several of their crystal structures have been solved from X-ray diffraction data which show the molecules to be arranged in a variety of packing motifs. The compound 1,4-bis(4′-pyridylethynyl)tetrafluorobenzene has been shown by differential thermal analysis and transmitted polarised light microscopy to exhibit, at high temperature, a hexagonal phase which could be either a hexatic B mesophase or a crystal B phase. High-temperature X-ray diffraction studies are required to establish which is the case. In addition, a 1 : 1 coordination polymer of 1,4-bis(4′-pyridylethynyl)tetrafluorobenzene with zinc(II) nitrate has been obtained in which the ligands are arranged in infinite zig-zag chains linked by the metal centres. Future work will concentrate on obtaining the crystal structures and evaluating the properties of new coordination polymers from these ligands in combination with other metal salts.

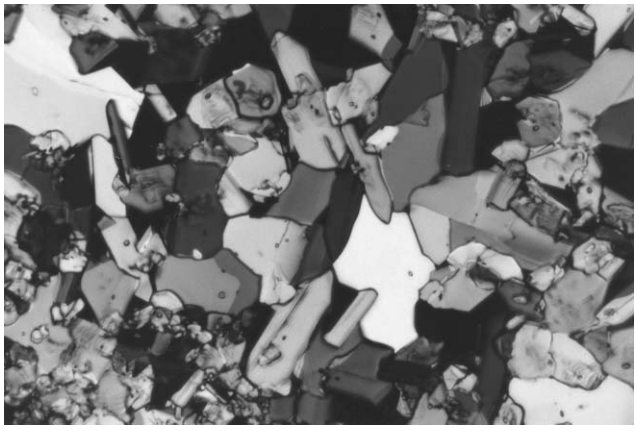


Fig. 8 The texture of the crystal B or hexatic B phase of **1b** viewed by transmitted polarised light microscopy. Image shows 50.33 μm by 33.66 μm region of sample.

Experimental

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. The solvents diethylamine, diisopropylamine and triethylamine were freshly distilled from CaH_2 under nitrogen prior to use. NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer operating at 200 MHz for ^1H and 188 MHz for $^{19}F\{^1H\}$. Proton chemical shifts are relative to TMS and referenced against residual $CHCl_3$ as the internal standard; ^{19}F chemical shifts are referenced to external $CFCl_3$. Chemical shifts are reported in ppm and coupling constants in Hz. FT-IR spectra were recorded from Nujol mulls on a Perkin-Elmer 1600 FT-IR spectrophotometer. Absorption spectra were recorded on a Hewlett-Packard 8453 diode array UV-vis spectrophotometer in acetonitrile. Fluoresence spectra were measured on a Jobin-Yvon Fluoromax 3 spectrophotometer in acetonitrile. Elemental analyses were obtained from M-H-W Laboratories, Phoenix, Arizona and the University of Durham elemental analysis service. GC/MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a 5971A mass selective detector and a fused silica capillary column. The following operating conditions were used: injector 250 °C; detector 280 °C; oven temperature was ramped from 70 to 280 °C at a rate of 20 °C min^{-1}. UHP grade helium was used as the carrier gas. High resolution EI-MS was performed on a Micromass Autospec mass spectrometer. High resolution electrospray ionisation (ESI) mass spectrometry was performed on a Micromass LCT spectrometer running in high resolution ES+ mode. The compound 9,10-diiodoanthracene[22] and the terminal alkynes 4-ethynylpyridine,[23] 1,4-diethynylbenzene and 1,4-diethynyltetrafluorobenzene[24] were prepared by literature procedures, and all other reagents were obtained from commercial sources and used as received.

Synthesis of 1,4-bis(4′-pyridylethynyl)benzene (1a)

Diisopropylamine (80 mL) was added to a mixture of 4-ethynylpyridine (0.37g, 3.60 mmol), 1,4-diiodobenzene (0.51 g, 1.55 mmol), $PdCl_2(PPh_3)_2$ (0.018 g, 0.026 mmol) and CuI (0.005 g, 0.026 mmol). The reaction mixture was stirred for 2 h after which the solvent was removed *in vacuo*. The residue was dissolved in toluene and eluted through a column of alumina (4 cm). Removal of the toluene gave the desired compound as a white powder. Yield 0.26 g (60%). ^1H NMR (200 MHz) δ: 7.39 (4H, m, PyH), 7.56 (4H, s, ArH), 8.63 (4H, m, PyH). IR/cm^{-1}: 2220. MS (M+): *m/z* 280. Anal. calc. for $C_{20}H_{12}N_2$: C 85.69, H 4.31, N 9.99. Found: C 85.21, H 4.25, N 9.93%.

Synthesis of 1,4-bis(4′-pyridylethynyl)tetrafluorobenzene (1b)

Triethylamine (60 mL) was added to a degassed mixture of 4-ethynylpyridine (0.31 g, 3.00 mmol), 1,4-diiodotetrafluorobenzene (0.505 g, 1.25 mmol), $PdCl_2(PPh_3)_2$ (0.0175 g, 0.025 mmol) and CuI (0.0046 g, 0.025 mmol). The reaction mixture was heated to reflux for 4 h after which the solvent was removed *in vacuo*. The residue was dissolved in hot toluene and eluted through a column of alumina (4 cm). Cooling of the toluene solution gave the desired compound as pale yellow crystals. Yield 0.27 g (61%). ^1H NMR (200 MHz) δ: 7.46 (4H, m, PyH), 8.69 (4H, m, PyH). $^{19}F\{^1H\}$ NMR (188 MHz) δ: −132 (4F, s). IR/cm^{-1}: 2227. MS (M+): *m/z* 352. Anal. calc. for $C_{20}H_8F_4N_2$: C 68.18, H 2.27, N 7.95. Found: C 68.21, H 2.33, N 7.86%.

Synthesis of 1,4-bis(2′,3′,5′,6′-tetrafluoropyridylethynyl)benzene (1c)

A solution of 4-bromo-2,3,5,6-tetrafluoropyridine (0.69 g, 3.00 mmol) in triethylamine (20 mL) was added to a suspension of 1,4-diethynylbenzene (0.19 g, 1.50 mmol), $PdCl_2(PPh_3)_2$ (0.421 g, 0.060 mmol) and CuI (0.011 g, 0.060 mmol) in triethylamine (30 mL). The reaction mixture was heated to reflux for 3 h after which the solvent was removed *in vacuo*. The residue was dissolved in hot toluene and eluted through a column of alumina (4 cm). Cooling of the toluene solution gave the desired compound as a yellow solid. Yield 0.49 g (77%). ^1H NMR (200 MHz) δ: 7.66 (4H, s, ArH). $^{19}F\{^1H\}$ NMR (188 MHz) δ: −90.4 (4F, m, PyF), −138.3 (4F, m, PyF). IR/cm^{-1}: 2227. MS (M+): *m/z* 424. Anal. calc. for $C_{20}H_4F_8N_2$: C 56.62, H 0.95, N 6.60. Found: C 56.80, H 0.90, N 6.44%.

Alternative synthesis of 1,4-(4′-pyridylethynyl)tetrafluorobenzene (1c)

A solution of n-butyllithium in hexane (1.6 M, 6.25 mL, 10.0 mmol) was added dropwise to a solution of 1,4-diethynylbenzene (0.63 g, 5.0 mmol) in dry THF at −78 °C, and the reaction was stirred for 1 h. Pentafluoropyridine (1.69 g, 10.0 mmol) was added at −78 °C, and the solution was allowed to warm to room temperature and stirred for 16 h. The solvent was evaporated and the residue was filtered through a column of silica (4 cm) using hot toluene. The product crystallised as yellow needles upon cooling. Yield 0.85 g (34%).

Synthesis of 1,4-bis(2′,3′,5′,6′-tetrafluoropyridylethynyl)-tetrafluorobenzene (1d)

A solution of 4-bromo-2,3,5,6-tetrafluoropyridine (0.45 g, 2.00 mmol) in triethylamine (20 mL) was added to a suspension of 1,4-diethynyltetrafluorobenzene (0.17 g, 0.90 mmol), $PdCl_2(PPh_3)_2$ (0.026 g, 0.037 mmol) and CuI (0.007 g, 0.037 mmol) in triethylamine (30 mL). The reaction mixture was heated to reflux for 12 h after which the solvent was removed *in vacuo*. The residue was dissolved in hot toluene and eluted through a column of alumina (4 cm) with DCM/toluene. Yield 0.04 g (20%). $^{19}F\{^1H\}$ NMR (188 MHz) δ: −89.2 (4F, m, PyF), −133.5 (4F, s, ArF), −136.5 (4F, m, PyF). IR/cm^{-1}: 2229. HRMS (EI+): calc. for $C_{20}F_{12}N_2$ *m/z* 495.986987 found 495.987234.

Synthesis of 9,10-bis(4′-pyridylethynyl)anthracene (2) from 9,10-diiodoanthracene

Diisopropylamine (40 mL) was added to a Schlenk flask containing degassed mixture of 4-ethynylpyridine (0.09 g, 0.84 mmol) 9,10-diiodoanthracene (0.17 g, 0.40 mmol), $PdCl_2(PPh_3)_2$ (0.005 g, 0.008 mmol) and CuI (0.0015 g, 0.008 mmol). The reaction mixture was stirred overnight after which the solvent was removed *in vacuo*. The residue was dissolved in hexane/ethyl acetate and eluted through a column of alumina (4 cm). Yield 0.09 g (63%). ^1H NMR (200 MHz) δ: 7.63 (4H, d, J = 6 Hz, PyH), 7.71 (4H, m, ArH), 8.66 (4H, m, PyH), 8.73 (4H, d, J = 6 Hz, PyH). IR/cm^{-1}: 2205. HRMS (ESI: M + 1^+): calc. for $C_{28}H_{17}N_2$ *m/z* 381.1392 found 381.1413.

Synthesis of 9,10-bis(4′-pyridylethynyl)anthracene (2) from 9,10-dibromoanthracene

Triethyamine (40 mL) was added to a Schlenk flask containing a degassed mixture of 4-ethynylpyridine (0.40 g, 3.88 mmol) 9,10-dibromoanthracene (0.49 g, 1.46 mmol), and CuI (0.011 g, 0.057 mmol). In a nitrogen-filled glove-box, tri-*tert*-butylphosphine (0.023 g, 0.114 mmol) was added to $Pd(PhCN)_2Cl_2$ (0.022 g, 0.057 mmol) in dry, degassed toluene (1 mL). This solution was removed from the glove-box and added to the reaction mixture which was then stirred at room temperature for 24 h, after which the solvent was removed *in vacuo*. The residue was dissolved in hexane/ethyl acetate and eluted through a column of alumina (4 cm). Yield: 0.39 g (70%).

Synthesis of 4-(pentafluorophenylethynyl)pyridine (3a)

Dry triethylamine (100 mL) was added to a flask containing $Pd(PPh_3)_2Cl_2$ (0.03 g, 0.04 mmol), CuI (0.01 g, 0.04 mmol), and 4-ethynylpyridine (0.40 g, 4.0 mmol). Iodopentafluorobenzene (1.20 g, 4.0 mmol) was added and the reaction mixture was stirred at reflux for 6 h. The solvent was removed *in vacuo*, and the residue was dissolved in diethyl ether and eluted through a 3 cm alumina column, and recrystallised from petroleum ether 80/100 to give the product as an off-white solid. Yield 0.40 g (45%). Mp 123–124 °C. ^{1}H NMR (200 MHz) δ: 8.65 (2H, m, PyH), 7.42 (2H, m, PyH). ^{19}F{^{1}H} NMR (188 MHz) δ: −135.5 (2F, m, PhF), −151.0 (1F, m, PhF), −161.5 (2F, m, PhF). Anal. calc. for $C_{13}H_4F_5N$: C 58.01, H 1.50, N 5.20. Found: C 58.12, H 1.48, N 5.25%.

Synthesis of 4-(phenylethynyl)tetrafluoropyridine (3b)

A solution of n-butyllithium in hexanes (1.6 M, 6.25 mL, 10.0 mmol) was added dropwise to a solution of phenylacetylene (1.02 g, 10.0 mmol) in dry THF at −78 °C, and the solution was stirred for 1 h. Pentafluoropyridine (1.69 g, 10.0 mmol) was added to the solution at −78 °C, and the solution was allowed to warm to room temperature and stirred for 16 h. The solution was filtered through a column of silica (4 cm) using additional diethyl ether, and the filtrate was evaporated. The residue was dissolved in hexane and eluted through a silica column, and then recrystallised from hexane to give the pure compound as white needles. Yield 2.23 g (89%). Mp 104–105 °C. ^{1}H NMR (200 MHz) δ: 7.63 (2H, m, PhH), 7.46 (3H, m, PhH). ^{19}F{^{1}H} NMR (188 MHz) δ: −90.9 (2F, m, PyF), −138.7 (2F, m, PyF). Anal. calc. for $C_{13}H_5F_4N$: C 62.16, H 2.01, N 5.58. Found: C 62.35, H 2.04, N 5.47%.

Synthesis of (4), the coordination polymer of (1b) with $Zn(NO_3)_2$

A solution of $Zn(NO_3)_2{\cdot}6H_2O$ (0.05 g, 0.17 mol) in ethanol (10 mL) was carefully layered over a solution of **1b** (0.01 g, 0.028 mmol) in CH_2Cl_2 (10 mL). After 10 d, light yellow crystals suitable for X-ray diffraction were obtained at the interface between the layers and a precipitate formed at the bottom of the vial. After removal of a suitable crystal for diffraction, the remaining sample was filtered and the solid was washed with ethanol and CH_2Cl_2 to remove any unreacted starting materials. Yield 0.005g (45%).

X-Ray diffraction

Crystals of **1b** and **1c** were grown by slow cooling of hot toluene solutions, those of **2**, **3a** and **3b** by slow evaporation of ethyl acetate/hexane, hexane/DCM and hexane solutions, respectively. The X-ray diffraction experiment for **1b** was carried out on a 4-circle Rigaku AFC6S diffractometer with a point detector, using graphite-monochromated Cu-Kα radiation. Reflection intensities were measured in $2\theta/\omega$ scan mode and integrated using teXsan software.[25]

The experiments for **1c**, **2**, **3a** and **3b** were carried out on Bruker 3-circle diffractometers with SMART 6K (for **1c**) or SMART 1K (for **2**, **3a**, **3b**) CCD area detectors, using graphite-monochromated sealed-tube Mo-Kα radiation. The experiment for **4** was carried out on a Bruker 3-circle diffractometer with a ProteumM (APEX) CCD area detector, using graphite-monochromated Mo-Kα radiation from a 60 W Mo-target microfocus Bede Microsource® X-ray generator with glass polycapillary X-ray optics. Full spheres of the reciprocal space were scanned by several sets of narrow (0.3°) ω scans, each set with different (stationary) φ and 2θ angles. The low temperature of the crystals was maintained using Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. Reflection intensities were integrated using the SAINT program.[26]

The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL[27] software. All C, F and N atoms were refined in anisotropic approximation, all H atoms in isotropic approximation. The crystal of **1c** was a pseudo-merohedral twin, with the components related by rotation around the [1 0 2] axis and the reflections overlapping only partially. The intensity contribution from the second crystal was estimated at 6.1(1)%. The absolute configuration of **3b** was not determined. Crystal data and experimental details are listed in Table 4.

CCDC reference numbers 235646–235651.

See http://www.rsc.org/suppdata/jm/b4/b405128a/ for crystallographic data in CIF or other electronic format.

Differential thermal analysis (dta)

A Mettler FP900 Thermosystem, consisting of a Mettler FP90 control processor linked to an FP84 sample hot stage, was used to locate possible mesophase transitions in samples having an approximate mass of 5 mg. The calorimeter was calibrated with an indium standard. Experiments were conducted in an

Table 4 Crystallographic data and refinement parameters

Compound	**1b**	**1c**	**2**	**3a**	**3b**	**4**
Formula	$C_{20}H_8F_4N_2$	$C_{20}H_4F_8N_2$	$C_{28}H_{16}N_2$	$C_{13}H_4F_5N$	$C_{13}H_5F_4N$	$C_{20}H_8F_4N_4O_6Zn$
Formula weight	352.28	424.25	380.43	269.17	251.18	541.67
T/K	150(2)	110(2)	160(2)	120(2)	120(2)	120(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)	$P2_12_12_1$ (no. 19)	$P2/c$ (no. 13)
a/Å	5.787(1)	8.920(2)	11.045(1)	5.834(2)	5.031(1)	11.732(1)
b/Å	10.556(1)	5.060(1)	23.945(3)	8.965(3)	8.831(3)	5.274(1)
c/Å	13.112(1)	18.101(4)	7.248(1)	11.009(4)	23.579(7)	16.526(2)
α/°	90	90	90	71.17(1)	90	90
β/°	102.58(1)	91.93(3)	96.940(3)	82.05(1)	90	96.428(5)
γ/°	90	90	90	80.99(1)	90	90
V/Å^3	781.7(2)	816.5(3)	1902.8(4)	535.9(2)	1047.7(6)	1016.0(2)
Z	2	2	4	2	4	2
$\rho_{calc.}$/g cm^{-3}	1.497	1.726	1.328	1.668	1.591	1.771
λ/Å	1.54178	0.71073	0.71073	0.71073	0.71073	0.71073
μ/mm^{-1}	1.06	0.17	0.08	0.16	0.14	1.29
$2\theta_{max}$/°	150	60	56.6	61	58	58
Total reflections	1927	10667	5808	7323	11716	7359
Unique reflections	1542	2373	2176	3206	1648	2702
R_{int}	0.018	0.044	0.026	0.053	0.055	0.019
Reflections $I > 2\sigma(I)$	1430	1679	1779	1621	1548	2484
Parameters	135	144	142	188	183	159
R [F, $I > 2\sigma(I)$]	0.036	0.067	0.037	0.050	0.037	0.029
wR (F^2, all data)	0.108	0.254	0.117	0.137	0.084	0.077

environment of dry nitrogen, delivered through a cold finger at a flow rate of *ca.* 30 mL min^{-1}. Thermographs were displayed on a PC and analysed using Mettler FP99 system software (version 1). All heating and cooling operations were carried out at 10 °C min^{-1} and the onset temperature was determined for all transitions.

Prior to loading, the samples were crushed to a fine powder using a mortar and pestle. Aluminium sample and reference pans (25 μL) were hermetically sealed with aluminium lids using a Perkin-Elmer press to give a cold weld capable of withstanding pressures of up to 2 atm. Sample analysis was conducted as follows: the pan containing the sample was weighed and then placed in the appropriate compartment of the dta; sample and reference pans were equilibrated at 50 °C; both were heated, at 10 °C min^{-1}, to at least 5 °C above the sample's clearing/degradation temperature and cooled to 50 °C at the same rate before finally being returned to ambient temperature; the sample pan was then re-weighed. This sequence was carried out six times for each sample.

Transmitted polarised light microscopy (tplm)

An Olympus BH-2 transmitted polarised light microscope was used to examine the phase transitions detected by differential thermal methods. A Linkam THMS 600 heating/freezing stage and TP 92 temperature programmer/controller were used to enable observation of sample microstructures *in situ* at elevated temperatures.

The microscopy procedure for identifying phase transitions was as follows: samples in powder form were held between BDH borosilicate coverslips (22 mm × 22 mm; thickness no.1). The glass was first cleaned by immersing in concentrated nitric acid for 1 h, followed by thorough rinses in de-ionised water and then acetone. Following this, the clean coverslips were air-dried under a dust cover. Heating and cooling rates of 10 °C min^{-1} were typical and a dry nitrogen purge was provided through the sample chamber at *ca.* 30 mL min^{-1} in an attempt to limit sample oxidation. In the case of compound **1b**, heating rates of 0.5 °C min^{-1} were employed to resolve a crystal to crystal B/hexatic B transition, the phase transformation of which was also estimated from this run.

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References

1 (*a*) J.-M Lehn, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1304 1989, **29**, 190; (*b*) M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645; (*c*) M. Fujita and K. Ogura, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 1471; (*d*) R. V. Slone, J. T. Hupp, C. L. Stern and T. E. Albercht-Schmitt, *Inorg. Chem.*, 1996, **35**, 4096; (*e*) B. Olenyuk, J. A. Whiteford and P. J. Stang, *J. Am. Chem. Soc.*, 1996, **118**, 8221; (*f*) P. N. W. Baxter, G. S. Hanan and J.-M. Lehn, *Chem. Commun.*, 1996, 2019; (*g*) O. M. Yaghi, H. Li, C. Davis, D. Richardson and T. L. Groy, *Acc. Chem. Res.*, 1998, **31**, 474.

2 (*a*) A. J. Blake, N. R. Champness, P. Hubberstey, W. S. Li, M. A. Witherby and M. Schroder, *Coord. Chem. Rev.*, 1999, **183**, 117; (*b*) N. L. Rosi, M. Eddaoudi, J. Kim, M. O'Keeffe and O. M. Yaghi, *CrystEngComm*, 2002, **4**, 401; (*c*) B. Moulton and M. J. Zaworotko, *Curr. Opin. Solid State Mater. Sci.*, 2002, **6**, 117; (*d*) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469; (*e*) S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276.

3 (*a*) R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 1677; (*b*) S. Kawata, S. Kitagawa, M. Kondo, L. Furuchi and M. Munakata, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1759; (*c*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Chem. Commun.*, 1994, 2755; L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1997, 1801; (*d*) O. M. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1995, **117**, 10401; (*e*) M. L. Hernandez, M. G. Barandika, M. K. Urtiaga, R. Cortes, L. Lezama, M. I. Arriortua and T. Rojo, *J. Chem. Soc., Dalton Trans.*, 1999, 1401; (*f*) M. A. S. Goher and F. A. Mautner, *Polyhedron*, 1999, **18**, 1805; (*g*) C. B. Aakeroy, A. M. Beatty and D. S. Leinen, *Angew. Chem., Int. Ed.*, 1999, **38**, 1815; (*h*) L.-P. Zhang, W.-J. Lu and T. C. W. Mak, *Polyhedron*, 2004, **23**, 169.

4 (*a*) R. V. Slone, K. D. Benkstein, S. Belanger, J. T. Hupp, I. A. Guzei and A. L. Rheingold, *Coord. Chem. Rev.*, 1998, **171**, 221; (*b*) T. Rajendran, B. Manimaran, F.-Y. Lee, G.-H. Lee, S.-M. Peng, C. M. Wang and K.-L. Lu, *Inorg. Chem.*, 2000, **39**, 2016; (*c*) S. S. Sun and A. J. Lees, *J. Am. Chem. Soc.*, 2000, **122**, 8956; (*d*) C. Janiak, *Dalton Trans.*, 2003, 2781.

5 (*a*) M. Fujita and K. Ogura, *Coord. Chem. Rev.*, 1996, **148**, 249; (*b*) P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed.*, 1999, **38**, 2638.

6 (*a*) X.-M. Chen, M.-M. Tong, Y.-J. Luo and Z.-N. Chen, *Aust. J. Chem.*, 1996, **49**, 835; (*b*) J. Lu, T. Paliwala, S. C. Linn, C. Yu, T. Niu and A. J. Jacobson, *Inorg. Chem.*, 1997, **36**, 923; (*c*) A. J. Blake, S. J. Hill, P. Hubberstey and W.-S. Li, *J. Chem. Soc., Dalton Trans.*, 1997, 913; (*d*) M.-M. Tong, X.-M. Chen, X.-L Yu and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1998, 5; (*e*) M.-L. Tong, B.-H. Ye, J.-W. Cai, X.-M. Chen and S. W. Ng, *Inorg. Chem.*, 1998, **37**, 2645; (*f*) K. Biradha, K. V. Domasevitch, B. Moulton, C. Seward and M. J. Zaworotko, *Chem. Commun.*, 1999, 1327; (*g*) S.-L. Noro, M. Kondo, T. Ishii, S. Kitagawa and H. Matsuzaka, *J. Chem. Soc., Dalton Trans.*, 1999, 1569; (*h*) S. A. Barnett and N. R. Champness, *Coord. Chem. Rev.*, 2003, **246**, 145.

7 (*a*) A. J. Blake, N. R. Champness, A. Khlobystov, D. A. Lemenovskii, W. S. Li and M. Schroder, *Chem. Commun.*, 1997, 2027; (*b*) L. Carlucci, G. Ciani and D. M. Proserpio, *Chem. Commun.*, 1999, 449; L. Carlucci, G. Ciani and D. M. Proserpio, *J. Chem. Soc., Dalton Trans.*, 1999, 1799; (*c*) K. Biradha and M. Fujita, *J. Chem. Soc., Dalton Trans.*, 2000, 3805; (*d*) A. J. Blake, G. Baum, N. R. Champness, S. S. M. Chung, P. A. Cooke, D. Fenske, A. Khlobystov, D. A. Lemenovskii, W. S. Li and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 2000, 4285; (*e*) M. B. Zaman, M. D. Smith and H. C. zur Loye, *Chem. Commun.*, 2001, 2256; (*f*) T. Rajendran, B. Manimaran, R.-t. Liao, T. Ren-Jay, P. Thanasekaran, G.-H. Lee, S.-M. Peng, Y.-H. Liu, I. Chang, S. Rajagopal and K.-L. Lu, *Inorg. Chem.*, 2003, **42**, 6388; (*g*) M. Ferrer, M. Mounir, O. Rossell, E. Ruiz and M. A. Maestro, *Inorg. Chem.*, 2003, **42**, 5890; (*h*) M. Fujita, O. Sasaki, T. Mitsuhashi, T. Fujita, J. Yazaki, K. Yamaguchi and K. Ogura, *Chem. Commun.*, 1996, 1535; (*i*) N. G. Pschirer, D. M. Ciurtin, M. D. Smith, U. H. F. Bunz and H. C. zur Loye, *Angew. Chem., Int. Ed.*, 2001, **41**, 583.

8 O. Ohmori, M. Kawano and M. Fujita, *CrystEngComm.*, 2004, **6**, 51.

9 (*a*) M. Fujita, S. Nagao, M. Iida, K. Ogata and K. Ogura, *J. Am. Chem. Soc.*, 1993, **115**, 1574; (*b*) K. Kasai, M. Aoyagi and M. Fujita, *J. Am. Chem. Soc.*, 2000, **122**, 2140.

10 (*a*) R. D. Chambers, C. W. Hall, J. Hutchinson and R. W. Millar, *J. Chem. Soc., Perkin Trans. 1*, 1998, 1705; (*b*) R. D. Chambers, P. R. Hoskin, G. Sandford, D. S. Yufit and J. A. K. Howard, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2788; (*c*) H. Benmansour, R. D. Chambers, P. R. Hoskin and G. Sandford, *J. Fluorine Chem.*, 2001, **112**, 133; (*d*) I. V. Alabugin and S. V. Kovalenko, *J. Am. Chem. Soc.*, 2002, **124**, 9052.

11 (*a*) S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627; (*b*) J. Suffert and R. Ziessel, *Tetrahedron Lett.*, 1990, **32**, 757; (*c*) P. Nguyen, S. Todd, D. Van den Biggelar,

N. J. Taylor, T. B. Marder, F. Wittman and R. H. Friend, *Synlett.*, 1994, 299.

12 (*a*) P. L. Coe, J. C. Tatlow and R. C. Terrell, *J. Chem. Soc., Sect. C*, 1967, 2626; (*b*) M. R. Wiles and A. G. Massey, *Tetrahedron Lett.*, 1967, 5137.

13 (*a*) P. Nguyen, Z. Yuan, L. Agocs, G. Lesley and T. B. Marder, *Inorg. Chim. Acta*, 1994, **220**, 289; (*b*) J.-T. Lin, S.-S. Sun, J. J. Wu, L. Lee, K.-J. Lin and Y. F. Huang, *Inorg. Chem.*, 1995, **34**, 2323; (*c*) A. J. Amoroso, A. M. W. C. Thompson, J. P. Maher, J. A. McCleverty and M. D. Ward, *Inorg. Chem.*, 1995, **34**, 4828; (*d*) N. R. Champness, A. Khlobystov, A. G. Majuga, M. Schroder and N. V. Zyk, *Tetrahedron Lett.*, 1999, **40**, 5413.

14 T. Hundermark, A. F. Littke, S. L. Buchwald and G. C. Fu, *Org. Lett.*, 2000, **2**, 1729.

15 (*a*) G. A. Artamkina, S. V. Kovalenko, I. P. Beletskaya and O. A. Reutov, *Zh. Org. Khim.*, 1990, **26**, 225 (*J. Org. Chem. USSR,* 1990, **26**, 187) (English translation)

16 (*a*) S. V. Larionov, L. A. Glinskaya, T. G. Leonova and R. F. Klevtsova, *Koord. Khim.*, 1998, **24**, 909 (in Russian); (*b*) J. T. Sampanthar and J. J. Vittal, *J. Chem. Soc., Dalton Trans.*, 1999, 1993; (*c*) L. A. Glinskaya, V. G. Shchukin, R. F. Klevtsova, A. N. Mazhara and S. V. Larionov, *Zh. Strukt. Khim.*, 2000, **41**, 772 (in Russian); (*d*) W. Li, M.-L. Tong, X.-M. Chen and S. W. Ng, *Main Group Met. Chem.*, 2001, **24**, 799; (*e*) J. J. Vittal, J. T. Sampanthar and Z. Lu, *Inorg. Chim. Acta*, 2003, **343**, 224.

17 R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384.

18 (*a*) C. E. Smith, P. S. Smith, R. Ll. Thomas, E. G. Robins, J. C. Collings, C. Dai, A. J. Scott, S. Borwick, A. S. Batsanov, S. W. Watt, S. J. Clark, C. Viney, J. A. K. Howard, W. Clegg and T. B. Marder, *J. Mater. Chem.*, 2004, **14**, 413; (*b*) G. W. Coates, A. R. Dunn, L. M. Henling, J. W. Ziller, E. B. Lobkovsky and R. H. Grubbs, *J. Am. Chem. Soc.*, 1998, **120**, 3641; (*c*) G. W. Coates, A. R. Dunn, L. M. Henling, D. A. Dougherty and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 248; (*d*) C. Dai, P. Nguyen, T. B. Marder, A. J. Scott, W. Clegg and C. Viney, *Chem. Commun.*, 1999, 2493; (*e*) S. W. Watt, C. Dai, A. J. Scott, J. M. Burke, R. Ll. Thomas, J. C. Collings, C. Viney, W. Clegg and T. B. Marder, *Angew. Chem., Int. Ed., in press, manuscript number Z53828; (f)* F. Ponzini, R. Zagha, K. Hardcastle and J. S. Seigel, *Angew. Chem., Int. Ed.*, 2000, **39**, 2323; (*g*) G. P. Bartholomew, G. C. Bazan, X. Bu and R. J. Lachicotte, *Chem. Mater.*, 2000, **12**, 1422; (*h*) G. P. Bartholomew, X. Bu and G. C. Bazan, *Chem. Mater.*, 2000, **12**, 2311; (*i*) W. J. Feast, P. W. Lovenich, H. Puschmann and C. Taliani, *Chem. Commun.*, 2001, 505; (*j*) V. R. Vangala, A. Nangia and V. M. Lynch, *Chem. Commun.*, 2002, 1305; (*k*) See also: U. H. F. Bunz and V. Enkelmann, *Chem. Eur. J.*, 1999, **5**, 263.

19 (*a*) G. R. Desiraju and A. Gavezzotti, *J. Chem. Soc., Chem. Commun.*, 1989, 621; (*b*) G. R. Desiraju and A. Gavezzotti, *Acta Crystallogr., Sect. B*, 1989, **45**, 473.

20 See, for example: (*a*) J. C. Collings, K. P. Roscoe, E. G. Robins, A. S. Batsanov, L. M. Stimson, J. A. K. Howard, S. J. Clark and T. B. Marder, *New J. Chem.*, 2002, **26**, 1740; (*b*) J. C. Collings, K. P. Roscoe, R. Ll. Thomas, A. S. Batsanov, L. M. Stimson, J. A. K. Howard and T. B. Marder, *New J. Chem.*, 2001, **25**, 1410 and references therein.

21 (*a*) R. Resel, P. Thurner, H. Kahlert, H. Vollenkle, B. Winkler, R. Mullner, F. Stelzer, D. Tunega and G. Leising, *Acta Crystallogr., Sect. C*, 1999, **55**, 693; (*b*) R. G. Pritchard, *Acta Crystallogr., Sect. C*, 1987, **43**, 129; (*c*) R. E. Banks, I. M. Farhat, R. Fields, R. G. Pritchard and M. H. Saleh, *J. Fluorine Chem.*, 1985, **28**, 325.

22 B. F. Duerr, Y. S. Chung and A. W. Czarnik, *J. Org. Chem.*, 1988, **53**, 2120.

23 (*a*) L. D. Ciana and A. Haim, *J. Heterocycl. Chem.*, 1984, **21**, 607; (*b*) J. G. Rodriguez, R. Martin-Villamil, F. H. Cano and I. Fonesca, *J. Chem. Soc., Perkin Trans. 1*, 1998, 709.

24 T. X. Neenan and G. M. Whitesides, *J. Org. Chem.*, 1988, **53**, 2489.

25 *TEXSAN, version 5.1*, Molecular Structure Corporation, Woodlands, Texas, USA, 1989.

26 *SAINT, version 6.02A*, Bruker AXS, Madison, Wisconsin, USA, 2001.

27 *SHELXTL, version 5.10*, Bruker AXS, Madison, Wisconsin, USA, 1997.