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Mesogenic, trimeric, halogen-bonded complexes from alkoxystilbazoles and 1,4-diiodotetrafluorobenzene†

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New, halogen-bonded mesogens are formed as trimeric complexes of two molecules of alkoxystilbazole and one of 1,4-diiodotetrafluorobenzene. The pure complexes show only monotropic nematic phases, while mixtures show a enantiotropic nematic with a range of up to 11 °C. A possible correlation between nematic phase stability and halogen bond strength is suggested.

Introduction

Liquid crystal mesophases are formed by the self assembly of anisometric molecules into anisotropic, fluid phases whose physical properties are of particular interest in the formation of functional materials.[1] These soft materials can organise into a range of structures that are implicated not only in the highly profitable display industry, but also in a wide range of other, non-display arenas.[2]

In the conventional design of calamitic liquid crystals, it is often the case that a fairly rigid, rod-like moiety is bound to a flexible, terminal chain, and such molecules are able to assemble into a wide range of mesophases with differing degrees of order. The covalent incorporation of fluorinated groups represents an efficient strategy to enhance both physical properties and to exert control over supramolecular organisation.[3] For example, lateral fluorination of a calamitic core can lead to a great degree of control over mesophase type and transition temperature, while the use of perfluorinated terminal chains tends to result in higher transition temperatures (compared to hydrocarbon analogues), the dominance of the SmA phase and the effective absence of nematic phases.[4,5]

During the past two decades, supramolecular chemistry has made significant advances in the formation of well-defined structures by exploiting weak, non-covalent interactions.[6] Thus, these non-covalent interactions (*e.g.* hydrogen bonding, charge-transfer and quadrupolar interactions) are able to induce liquid crystallinity from non-mesomorphic components.[7] As an analogue of the hydrogen bond, the halogen bond, namely any non-covalent interaction involving halogens as electrophilic species, is emerging as a new and useful tool in the array of such weak interactions.[8] From a conceptual point of view, halogen bonding has demonstrated its efficiency and reliability in the construction of complicated supramolecular architectures.[9] Moreover, the first applications have been performed in fields as diverse as [2 + 2] photoaddition reactions in the solid state, non-linear optics, formation of interpenetrated networks and the resolution of a racemate.[10]

Recently, some of us have reported that halogen bonding could induce liquid crystal behaviour from non-mesomorphic alkoxystilbazole and iodopentafluorobenzene.[11] This initial work has opened new perspectives in the engineering of liquid crystals and, for example, later work involving difunctional molecules has provided the first halogen-bonded, liquid-crystalline polymers, which exhibited nematic phases.[12]

Two subsequent papers, however, showed how trimeric systems may be constructed using a difunctional iodo electron-acceptor (Fig. 1).[13] Thus, some of us showed[13a] how α,ω-diiodoperfluoroalkanes hold together two stilbazoles (Fig. 1, **1**) and that despite the clear segregation of the fluorinated fragments in the crystal phase, the mesophases were all nematic. Subsequently, Xu *et al.* reported[13b] trimeric materials (Fig. 1, **2**) in which two tetrafluoroiodobenzene units were held together by a flexible methylene chain, which was bound subsequently to stilbazoles. The mesomorphism of these materials was dominated by the formation of SmA phases.

Keen to explore the potential of halogen bonding in the formation of liquid crystal materials, we extended our studies to new trimeric systems based on difunctional halobenzenes (Fig. 2, **3** to **5**). In particular, we concentrated on the use of 1,4-diiodotetrafluorobenzene (DITFB) as typical of a more conventional halogen bond-donor (electron-acceptor, Lewis acid), although for the purposes of comparison, we also looked at 1,4-dibromotetrafluorobenzene (DBrTFB) and 1,4-diiodobenzene.

Results and discussion

Complexation was attempted in these systems by co-crystallising, from THF, 4-alkoxy-4′-stilbazoles with the halogen bond-donor in a 2 : 1 ratio. After slow evaporation of THF,

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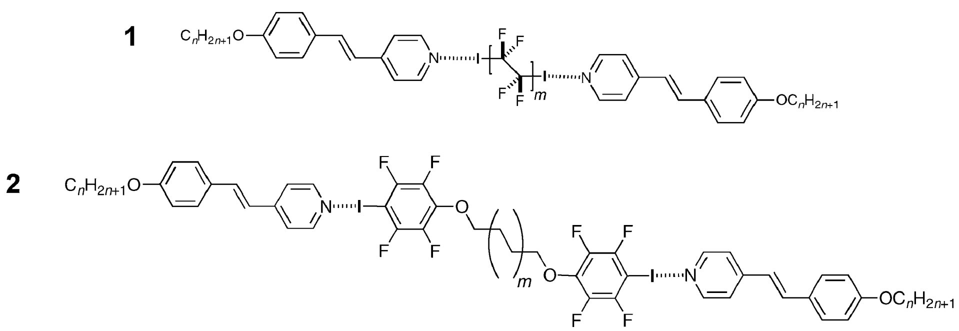

Fig. 1 Previously reported trimeric, halogen-bonded liquid crystals.[13b]

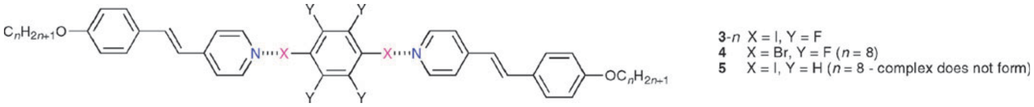

Fig. 2 General structure of the complexes studied.

pale yellow crystals were recovered in the cases of the dihalotetrafluorobenzenes, the change in colour (the components are colourless) reflecting the perturbation of the HOMO–LUMO transition of the stilbazole by the interaction of the nitrogen with a δ^+ acceptor.[14] No evidence of complexation was ever observed when using 1,4-diiodobenzene, as expected when considering that the iodine atoms are less electron-poor than in the diiodotetrafluorobenzene.[15]

For **3**-8 and **4**, we were able to obtain single crystals and so confirm the 2 : 1 nature of the complex (*vide infra*). In order to verify that the 2 : 1 ratio of species observed in the single crystals is also representative of the entire sample, we obtained ^1H and ^{19}F NMR data using 1*H*,6*H*-perfluorohexane as an internal standard that contained both hydrogen and fluorine nuclei. The integration parameters were set so that, in the ^1H NMR spectra, the triplet of triplets at δ 6.05 of the two terminal hydrogens of the standard corresponded to two and in the ^{19}F NMR spectra each of the $-CF_2-$ signals corresponded to four. By calculating ratios in each spectrum, it was possible to show that the ratio between the integral of the $-CH_3$ signal of the stilbazole and the aromatic C*F* fluorines was 1.5, showing the 2 : 1 nature of the stilbazole–1,4-dihalotetrafluorobenzene complex.

Furthermore, ^{19}F NMR studies have shown a high-field shift $\Delta\delta_F = 0.11$, where $\Delta\delta$ is defined as $\Delta\delta_F = \delta(\text{pure } C_6F_4I_2) - \delta(C_6F_4I_2 \text{ complex})$, for the aromatic C*F* fluorines of the diiodide module in the trimeric system **3**-8 (0.3 M solution). The ^{19}F NMR spectrum of the dibromide module in complex **4** also showed a change in the chemical shift, the only difference was that shift change was considerably smaller, consistent with the fact that bromoperfluoroarenes are weaker halogen bonding-donors than iodoperfluoroarenes.[9] Clearly, these shifts result from the specific nature of halogen bonding in this system rather than non-specific solute–solute interactions. Full NMR data and spectra are reported in the ESI.†

The single crystal structure of **3**-8 provided information on the trimeric arrangements (Table 2, Fig. 3a and b).‡ Thus, the diiodotetrafluorobenzene acts as a bidentate halogen bond-donor and is pinned to its binding sites by two stilbazoles which act, in turn, as monodentate electron-donors. The distance between the nitrogen and the iodine is 2.812 Å, which is some 20% less than the sum of the van der Waals' radii of N and I, while the N···I–C angle is almost linear at 175.09°, confirming the n → σ* character of the interaction.[16] From a topological point of view, the system adopts a stepped organisation due to a conformational rotation of the aromatic ring with regard to the stilbazole modules (Fig. 3a and b).

While the nitrogenated groups of **3**-8 are perfectly coplanar, they are twisted with respect to the tetrafluorobenzene with an angle of 70°. Moreover, the undulating trimeric system arrangement presents an inversion centre sitting in the middle of the perfluoroarene. It is well-established that benzene and perfluorobenzene can adopt a face-to-face arrangement due to their large but opposite quadrupolar moments.[17] However, in these cases, the modules stack in separated columns and no such interactions are observed (Fig. 4).

The molecular packing arrangements within the crystals of **3**-8 (and **4**, *vide infra*) are virtually identical and are such that the diiodoperfluoroarene and stilbazole molecules are segregated (Fig. 4). The stilbazoles are stacked with the aromatic rings parallel and alternating head-to-tail (*i.e.* with the alkyl side chain sandwiched between the aromatic rings and *vice versa*) (Fig. 5). The diiodobenzenes are positioned close to the pyridyl nitrogen of the stilbazole (and are halogen-bonded to it). The planes of the diiodobenzene rings are approximately perpendicular to the adjacent stilbazole rings and are aligned in columns. This coplanar alignment allows the fluorines of adjacent diiodobenzenes to be in close proximity with each other.

Infrared spectroscopy is also an effective tool for the investigation of halogen bonding interactions[18] through the study of vibrational motions in term of intensity and shift. In general, because halogen bonding is weaker than covalent or ionic bonds, it is reasonable to discuss vibrational spectra in terms of modified modes of starting compounds. Typical infrared features of halogen-bonded pyridine–iodoperfluoro arene complexes concern a blue-shift and intensity decrease in the pyridine bands in the region 3000–3100 cm^{-1}, and a red-

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‡ CCDC reference numbers 665553–665554. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709107a

Table 1 Thermal behaviour of complexes **3**-*n*, **4**, and mixtures

Complex	Transition	*T*/°C
3-6	Cr–I	129
	(N–I)	(113)
3-8	Cr–I	119–120
	(N–I)	(113.5)
3-10	Cr–I	115.7
	(N–I)	(109)
4	Cr–I	91–93
M1	Cr–N	110
	N–I	111.5
M2	Cr–N	100
	N–I	111.5

shift of the bands associated with the tetrafluorophenyl ring. In all of the complexes described in this paper, this behaviour is clearly satisfied, confirming the occurrence of halogen bonding. For instance, the $\nu_{\text{C–H}}$ absorption of the pure stilbazole at 3022 cm^{-1} becomes less intense in **3**-8 and is shifted to 3028 cm^{-1} as a result of a higher positive charge on the pyridyl hydrogens in the complex. Regarding the electron-acceptor components, the vibrations related to the fluorophenyl moiety at 1457, 940, and 758 cm^{-1} for the diiodotetrafluorobenzene are red-shifted to 1450, 935, and 754 cm^{-1}, respectively on complexation. Similar shifts are also observed for the complex **4** involving the dibromotetrafluorobenzene. Infrared spectra for all the investigated compounds are reported in the ESI.†

The liquid-crystalline properties of compounds **3**-*n* and **4** were examined by hot stage polarising optical microscopy and differential scanning calorimetry; thermal data are collected in Table 1. Thus, on heating, complexes **3**-*n* melted directly to the isotropic liquid, although on first heating, this melting event was rather broad and the sample appeared to show both isotropic liquid and crystalline solid. Puzzled by this observation, a couple of complexes were prepared in which the stilbazole and the diiodotetrafluorobenzene were mixed in a 1 : 1 ratio. From the observation of the thermal behaviour of these materials, it was clear that, despite the ratio at mixing, a 2 : 1 (stilbazole–diiodotetrafluorobenzene) complex had formed and that there was residual, uncomplexed diiodobenzene present. The rather broad melting event on first heating is then attributed to incomplete mixing/complexation on preparation. Indeed, we believe that simply mixing the different components does not guarantee 100% complex formation, an observation that is not uncommon in hydrogen-bonded systems where it is often necessary to melt the entire sample to ensure that complexation is complete. Such an assertion here is supported by the fact that cooling and subsequent heating behaviour is indicative of a single-component system.

On cooling from the isotropic state of the complexes, a monotropic nematic phase was seen clearly for **3**-8 and was sufficiently long-lived that a thermodynamic transition temperature of 113.5 °C could be measured.

Cooling **3**-6 and **3**-10 also led to monotropic nematic phases and, while more difficult to stabilise because of the often rapid onset of crystallisation, reliable, thermodynamic N–I transition temperatures of 113.0 and 109.0 °C, respectively, could be measured. DSC data could not, however, be collected for these monotropic transitions as crystallisation occurred before the mesophase formed. Such an apparent discrepancy is not

Table 2 Crystal data for complexes **3**-8 and **4**

Compound	**3**-8	**4**
Empirical formula	$C_{24}H_{27}F_2INO$	$C_{24}H_{27}BrF_2NO$
Formula weight/g mol^{-1}	510.37	463.38
T/K	110(2)	110(2)
λ/Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions/Å	$a = 7.6014(8)$	$a = 7.6549(7)$
	$b = 12.5366(13)$	$b = 12.1014(12)$
	$c = 13.2340(14)$	$c = 13.0598(13)$
Unit cell angles/°	$\alpha = 114.368(2)$	$\alpha = 109.606(2)$
	$\beta = 91.703(2)$	$\beta = 92.273(2)$
	$\gamma = 106.360(2)$	$\gamma = 107.571(2)$
Volume/Å^3	1086.8(2)	1073.01(18)
Z	2	2
ρ(calculated)/Mg m^{-3}	1.560	1.434
Absorption coefficient/mm^{-1}	1.505	1.947
F(000)	514	478
Crystal size/mm^3	0.34 × 0.10 × 0.03	0.27 × 0.20 × 0.05
θ range for data collection/°	1.71 to 28.31	1.68 to 29.99
Index ranges	$-10 <= h <= 10, -16 <= k <= 16, -17 <= l <= 17$	$-10 <= h <= 10, -16 <= k <= 17, -17 <= l <= 18$
Reflections collected	11 209	12 387
Independent reflections	5337 [*R*(int) = 0.0207]	6092 [*R*(int) = 0.0250]
Completeness to θ = 29.99°	98.8%	97.4%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.960 and 0.728	0.910 and 0.703
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5337/0/263	6092/0/263
Goodness-of-fit on F^2	1.056	1.072
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0237$, $wR_2 = 0.0557$	$R_1 = 0.0305$, $wR_2 = 0.0762$
R indices (all data)	$R_1 = 0.0276$, $wR_2 = 0.0570$	$R_1 = 0.0346$, $wR_2 = 0.0778$
Largest diff. peak and hole/e Å^{-3}	0.982 and −0.350	0.595 and −0.296

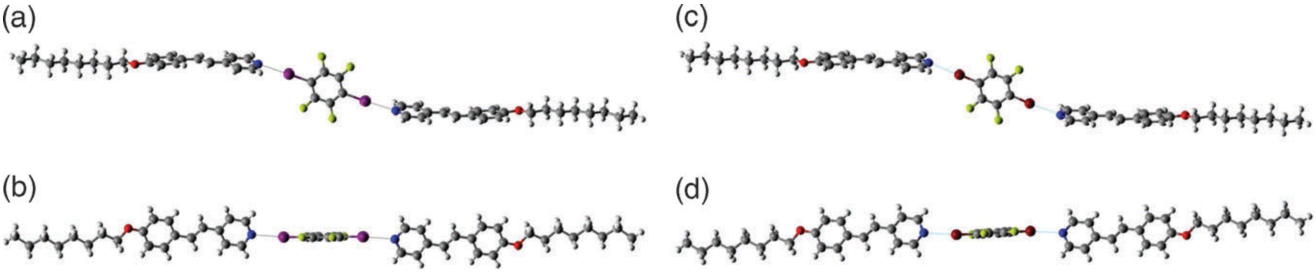

Fig. 3 X-Ray structures of trimeric systems **3**-8 (a, b) and **4** (c, d). (a) and (c): view along the crystallographic *c*-axis; (b) and (d): view along the crystallographic *a*-axis.

surprising as the DSC and microscopy experiments are different and the transition being sought is monotropic. Thus, while it can be stabilised in thin films on the microscope, this was not the case for a much larger sample in the DSC pan. No mesophase was observed for either **3**-4 or **3**-12.

Disappointed by the monotropic nature of the mesomorphism, a mixture (**M1**) was then prepared by heating together into the melt in a sealed vial, an equimolar (1 : 1 : 1) mixture of 4-hexyloxystilbazole, 4-decyloxystilbazole and 1,4-diiodo tetrafluorobenzene. Mixtures are a common feature of liquid crystals and are attractive, as melting points tend to be depressed while clearing points are a linear function of composition and the clearing points of the components, so that wide, liquid-crystalline ranges can be created. Prepared as it was, **M1** should contain a 1 : 1 : 2 mixture of **3**-6, **3**-10 and the non-symmetric complex with two, different stilbazoles at the two ends of the dihalide. On heating, the mixture showed an enantiotropic nematic phase (Fig. 6) with the solid melting at 110 °C and clearing at 111.4 °C—just enantiotropic. An identical result was obtained if a 1 : 1 mixture of **3**-6 and **3**-10 was heated into the melt and then characterised. Encouraged by this result, another mixture was prepared (**M2**) with even more components, namely 1 : 2 : 1 : 2 butyloxystilbazole–octyloxystilbazole–dodecyloxystilbazole–diiodotetrafluorobenzene—again mixed by melting in a vial. This mixture showed an enantiotropic nematic phase, melting at 99.9 °C and clearing at 111.5 °C.

Having these mixtures to hand, we then looked again at DSC traces, and that for **M1** is shown as Fig. 7. The broad transitions observed for these materials mean that the narrow nematic range on heating is not resolved, but T_{NI} is observed clearly on cooling. An interesting observation, and one that is remarked upon below, is that the molar enthalpy for this transition, at 8.8 kJ mol^{-1}, is much higher than might otherwise be expected for a nematic-to-isotropic transition, which would more normally be found at about 1 kJ mol^{-1}.

It is reported in halogen-bonded systems that the strength of interactions decreases with the polarisability of the halogen according to I > Br > Cl[15] and in the first reports of halogen-bonded mesogens, some of us concluded that while complexes between an alkoxystilbazole and bromopentafluorobenzene may have formed, any such complex was insufficiently stable to support mesophase formation. However, to pursue this further, we attempted to form a complex between octyloxy stilbazole and 1,4-dibromotetrafluorobenzene and found that it was possible to obtain single crystals (Fig. 3c and d).

Many features of the structure mirrored those found for **3**-8 so that the N···Br distance was 2.867 Å (longer than the average N–Br bond length (1.90 Å) but shorter than the sum of N and Br van der Waals radii by about 16%), while the linearity of the N···Br–C angle (174.11°) unequivocally demonstrated charge transfer between both species. In fact, comparison of the crystal data (Table 2) show the two crystals to be almost isomorphous.

Complex **4** melted at 91–93 °C, which was higher than the melting point of dibromotetrafluorobenzene at 78–81 °C. Given the reasonably isostructural nature of **3**-8 and **4**, there is little reason why **4** should not also have been mesomorphic, yet no mesophases were observed. We suggest that this is due to the weaker nature of the N···Br interaction, which is unable to persist in the molten phase.

Consideration of this behaviour for the bromo analogue and examination of the data from the clearing point of the nematic complexes **3**-*n* and mixtures **M1** and **M2** for the iodo materials raises another thought. In hydrogen-bonded mesogens, it has occasionally been argued that the clearing transition is driven by the rupture of the hydrogen bond. However, we believe that this is clearly not the case given the observation of hydrogen bonding in mesophases above 200 °C[19] and also more direct evidence from variable-temperature electronic spectroscopy, which showed clearly the presence of only the hydrogen-bonded complex at a SmA–I transition.[14]

Fig. 4 Crystal packing of complexes **3**-8 (left) and **4** (right). Segregation is observed in both structures.

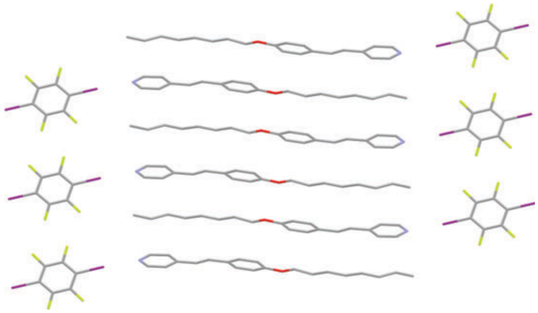

Fig. 5 The head-to-tail packing of the stilbazole units in the crystal structure of **3**-8 (hydrogen atoms omitted for clarity).

However, in the present work, the N–I transition appears relatively insensitive to stilbazole chain length. This leads to the suggestion that in these, halogen-bonded systems, rupture of the N···I interaction *may* contribute to the clearing process given that halogen bonds are, in our experience, much more labile than analogous hydrogen bonds and are more often weaker. Additional support for this assertion may possibly be drawn from the DSC data reported above. Thus, it was noted that $\Delta H(T_{NI})$ was close to 9 kJ mol^{-1}, whereas a much more typical value would be close to 1–2 kJ mol^{-1}. It is therefore tempting to consider that the additional enthalpy change is due to re-formation of the halogen bonds that were broken at clearing. However, such a proposition requires careful study that is beyond the scope of this work and so it is advanced as a tentative idea at this stage.

Experimental

Materials and methods

IR spectra were recorded with a Nicolet Nexus FT-IR spectrophotometer. Melting points were established with a Reichert instrument. DSC analysis was performed on a Linkam DSC 600 instrument with a heating rate of 10 °C min^{-1}. Commercially available chemicals were used without further purification. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker ADV 500 spectrometer at 25 °C; $CDCl_3$ was used as solvent, TMS and $CFCl_3$ were used as internal standards. NMR spectra were registered in the presence of 1*H*,6*H*-perfluorohexane as an internal standard. Chemicals were purchased from Sigma-Aldrich and Apollo Scientific.

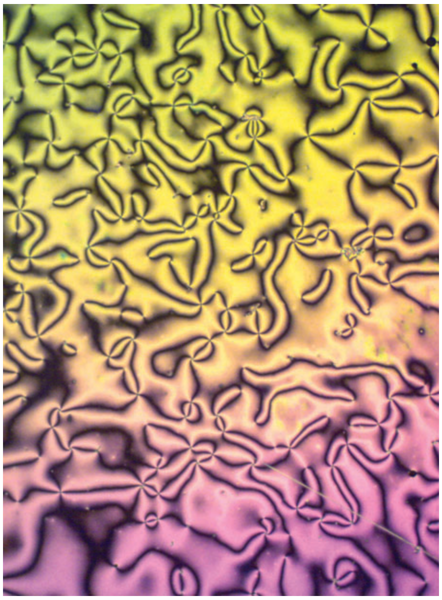

Fig. 6 Optical texture of the nematic phase of mixture **M1** at 110 °C on cooling from isotropic.

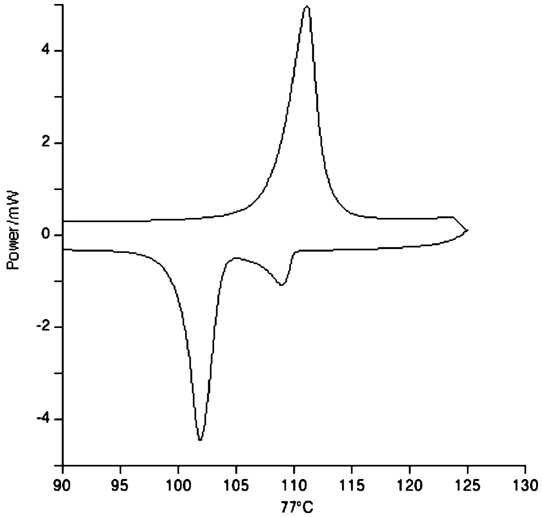

Fig. 7 DSC trace of mixture **M1** (10 K min^{-1}).

Analysis by X-ray diffraction. Single crystal X-ray structures were determined at 110 K using a Bruker SMART-APEX diffractometer equipped with CCDC area detector. The structures were solved using SHELXS-97 and refined with SHELXL-97.[20]

Formation of co-crystals 3-8 and 4. Two equivalents of 4-octyloxy-4′-stilbazole and one equivalent of 1,4-dihalotetrafluorobenzene were dissolved in THF at room temperature in a clear borosilicate glass vial. The open vial was placed in a closed cylindrical wide-mouth bottle containing paraffin. The THF was allowed to diffuse at room temperature.

Co-crystal **3**-*8*. Yellowish solid; mp 119–120 °C; IR: 4-octyloxy-4′-stilbazole ν_{max} = 3022, 2919, 2853, 1588, 1510, 1256, 824 cm^{-1}; 1,4-diiodotetrafluorobenzene: ν_{max} = 1457, 940, 758 cm^{-1}; co-crystal **3**-8: ν_{max} = 3028, 2922, 2848, 1593, 1514, 1450, 1260, 935, 827, 754 cm^{-1}.

Co-crystal **4**. Yellowish solid; mp 91–93 °C; IR: 1,4-dibromotetrafluorobenzene: ν_{max} = 1479, 952, 785 cm^{-1}; co-crystal **4**: ν_{max} = 3029, 2924, 2853, 1589, 1511, 1471, 1446, 1255, 948, 829, 785 cm^{-1}.

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