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Luminescent supramolecular assemblies based on hydrogen-bonded complexes of stilbenecarboxylic acids and dithieno[3,2-*b*:2′,3′-*d*]thiophene-2-carboxylic acids with a tris(imidazoline) base†

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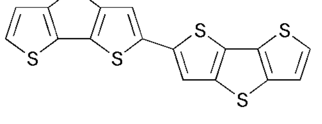
The synthesis of a number of stilbenecarboxylic acids, tetrazolylstilbenes and dithieno[3,2-*b*:2′,3′-*d*]thiophene-2-carboxylic acids is reported. These organic acids form non-covalent complexes with an imidazoline base, 1,3,5-tris(4,5-dihydroimidazol-2-yl)benzene **13**. Two X-ray crystal structures confirm hydrogen bonds between carboxylate ligands and *meta*-positioned protonated imidazoline groups. The complexes possess a surprisingly flat disk-like shape with various close contacts between adjacent molecules. Most stilbene and dithieno[3,2-*b*:2′,3′-*d*]thiophene derivatives show strong blue or blue–green photoluminescence in solution, whereas fluorescence in the solid state is almost completely quenched.

Introduction

There is currently great interest in the development of new organic and polymeric electronic materials, which can be spread easily over large areas and which are ideally suited for the manufacture of a range of thin-film devices, such as electroluminescent diodes and field-effect transistors.[1,2] Whereas low-molar-mass organic materials need to be sublimed for this purpose, conjugated polymers[1] and dendrimers[3] (highly branched molecules of defined molar mass) offer the potential of low-cost processing—typically by spin-coating or inkjet printing—from solution at room temperature. Both approaches give high quality thin films for device applications.

Materials for organic semiconductors and organic light-emitting diodes require high charge carrier mobilities under an applied electrical field to make charge transport efficient during device operation. High mobility is usually associated with a high degree of structural order and purity. Oligomers of thiophenes, such as the hexamer α-sexithiophene and the fused 2,2′-bi(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (BDT), are among the most promising examples. The thiophene hexamer yields single-crystalline films upon vacuum deposition of the highly purified compound under suitable conditions. Its quasi-planar molecules with a herringbone packing arrangement provide sufficient π-overlap between aromatic rings along the stacking axis.[4] The dimer of dithieno[3,2-*b*:2′,3′-*d*]thiophene is a related π-conjugated material that has been used successfully in organic field-effect transistors.[5] BDT exhibits a unique π-stacked structure in which the short distance between carbon atoms in two face-to-face oriented molecules is only 3.557 Å. A compressed molecular packing, strong intermolecular interactions and a wide HOMO–LUMO gap impart a high field-effect mobility (0.02–0.05 $cm^2 V^{-1} s^{-1}$) along the π−π stacking direction together with a high on/off ratio (up to 10^8) and sharp turn-on characteristics. Strong π-stacking is, however, also responsible for BDT's low solubility in most organic solvents; even for a dioctyl-substituted derivative solubility still remains at a level (2 $mg cm^{-3}$ in THF) too low for spin-coating.[6] Alternative dithienothiophene derivatives with good processibility were therefore sought.

Solution processing would clearly open up new avenues for non-polymeric charge-transporting and luminescent compounds in device applications. Although the solubility issue can be solved readily by the introduction of suitable solubilising groups, deposition of materials in a highly ordered form requires more. Supramolecular interactions have been considered as an alternative route towards ordered structures. A framework of hydrogen bonds has been responsible for controlling the stacking arrangement of dialkylbithiophenes functionalised with urea groups[7] whereas electrostatic interactions have played a key role in the preparation of self-assembled thin films by dip-deposition of alternating layers of polycationic and polyanionic polymers using a Langmuir–Blodgett-type technique.[8] In this way highly luminescent films have been obtained from water-soluble polymers containing oligophenylene and stilbene sequences. Likewise, supramolecular order in regioregular poly(3-hexylthiophenes) has been attributed to π-stacking interactions that are highly favourable in a well-defined regioregular conjugated polymer.[9] Another example by E. W. Meijer and co-workers describes the self-



BDT

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†Electronic supplementary information (ESI) available: packing views of the crystal structure of **14f**, preparation procedures and analytical data for **3*E***, **10*Z***, **12**, **18*E***, **27** and their corresponding complexes reported in this paper. See http://www.rsc.org/suppdata/jm/b0/b009406o/

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assembly of π-conjugated oligo(*p*-phenylenevinylenes) with a 2-ureidopyrimidin-4(1*H*)-one end group capable of dimer formation through self-complementary quadruple hydrogen-bonding.[10] Few liquid crystals have so far exhibited charge transport characteristics above 0.01 $cm^2\ V^{-1}\ s^{-1}$, since either a highly ordered crystal phase or extensive π-overlap seems to be crucial. Examples are 2-phenylnaphthalene[11a] or terthiophene[11b] (in the smectic *E*, *F* or *G* phase) and hexabenzocoronene derivatives (in a columnar hexagonal phase).[12]

We have recently devised a method that is capable of rendering chloroform-insoluble monocarboxylic (or heterocyclic) acids soluble in $CHCl_3$ and other non-polar solvents by complexation of the acid with a tris(imidazoline) base, such as **13**.[13,14] In the absence of protic co-solvents dissociation in solution is avoided, and all polar groups remain buried within the core of the complex. The introduction of additional solubilising groups along the periphery makes it possible for such complexes to possess—despite their hydrogen-bonded/salt-like structure—solubility in a range of non-polar solvents.

This paper describes how the concept can be applied to monocarboxylic acids of stilbenes and dithieno[3,2-*b*:2′,3′-*d*]thiophene, two types of compounds with a known propensity for high luminescence or charge transport mobility. We report details of the synthesis, crystal structures and optical properties of such hydrogen-bonded complexes.

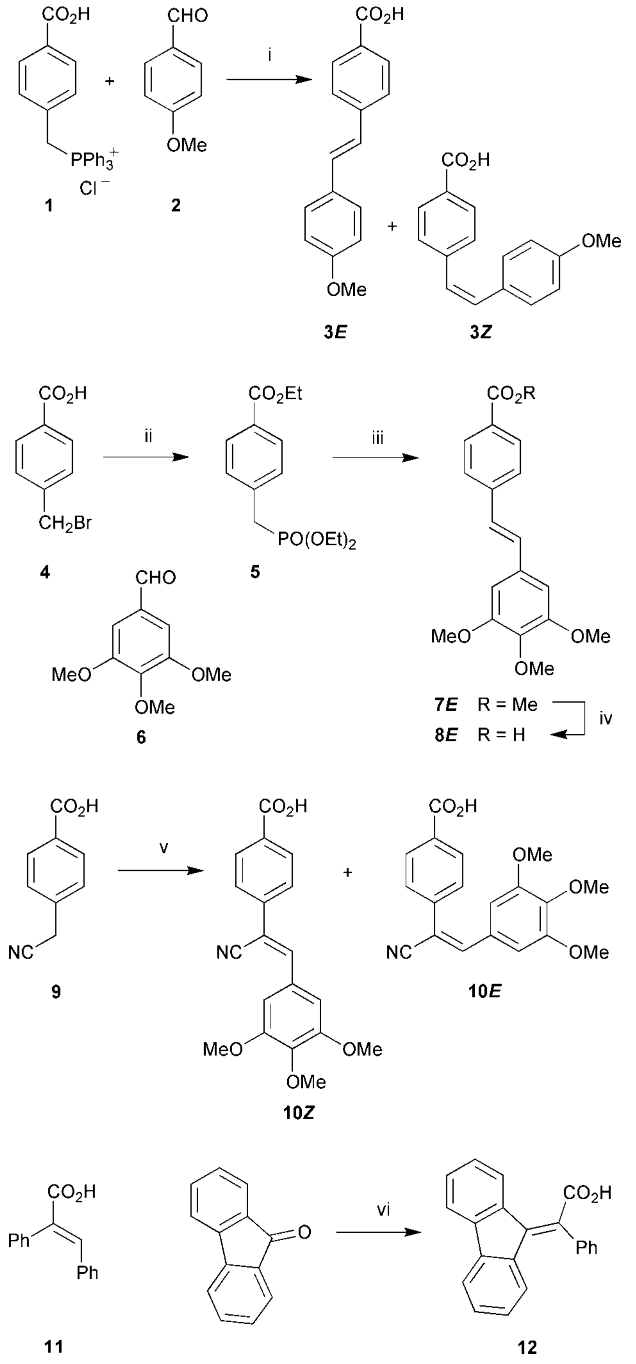
Results and discussion

Synthesis

Stilbene derivatives were chosen because of their established strong blue fluorescence and relatively straightforward synthesis. Each stilbene and dithienothiophene derivative was designed to have a single acidic functional group—typically a carboxylic acid or a tetrazole—which was required for hydrogen-bonding to tribasic core **13**.

A simple stilbenecarboxylic acid, such as **3**, was readily prepared by a Wittig reaction of 4-methoxybenzaldehyde with phosphonium salt **1**. Occasionally, mixtures of *trans* (**3*E***) and *cis* (**3*Z***) isomers were isolated as a result of a photochemical isomerisation of the *trans* compound (Scheme 1). So long as prolonged exposure of **3*E*** and especially of solutions of the compound to sunlight was avoided, the thermodynamically favoured (*E*)-stilbene derivative could be isolated as an isomerically pure compound after recrystallisation or gradient sublimation (Scheme 1).[15] Care had to be taken that compound **3**—as well as any of the other carboxylic or heterocyclic acids used in this study—was obtained in the protonated form without being contaminated by its corresponding sodium salt, which is an intermediate in the condensation reaction. When (*E*)-stilbenecarboxylic acid **3*E*** was combined with tris(imidazoline) base **13** in hot ethanol–chloroform, a 3 : 1 salt crystallised upon cooling (Scheme 2).‡ Complex **14a** did not dissolve in neat $CHCl_3$, and even after addition of MeOH its solubility remained below 2 mg cm^{-3}. Consequently, we decided to investigate possible routes to more soluble stilbene derivatives that would be more suitable for solution-processing techniques.

An obvious way of improving solubility is the introduction of long alkoxy side chain substituents. Apart from the more demanding task of purifying compounds of this type, long chain alkyl or alkoxy substituents 'dilute' the stilbene chromophore unnecessarily with paraffin-like groups; they are also liable to induce liquid-crystalline phases close to ambient temperature. Both features are generally avoided for device applications. We found that three methoxy substituents on the stilbene's peripheral phenyl group were surprisingly effective in preventing aggregation and promoting dissolution in chlorinated solvents at the same time. Since chromatographic removal of triphenylphosphine oxide resulted in unacceptably large losses during the purification of **3*E***, we abandoned Wittig reactions in favour of the Horner–Emmons variation that made work-up easier. Stilbene **8*E*** was thus prepared from 3,4,5-trimethoxybenzaldehyde **6** and phosphonate **5** followed by saponification of the intermediate ester **7*E***. The blue fluorescent complex **14b** possessed excellent solubility in $CHCl_3$ (up to 50 mg cm^{-3} at room temperature), which was considered to be sufficiently high for spin-coating applications.



Scheme 1 *Reagents and conditions*: i, NaOEt, EtOH, reflux, 1 h; ii, $P(OEt)_3$, reflux, 48 h; iii, **6**, Bu^{t}OK, THF, 25 °C, 24 h, then HCl; iv, KOH, EtOH, reflux, 3 h, then HCl; v, **6**, NaOEt, EtOH, reflux, 30 min, vi, $PhCH_2CO_2H$, NEt_3, Ac_2O, reflux, 15 h.

Several related derivatives were available through similar routes. Knoevenagel reaction of 3,4,5-trimethoxybenzaldehyde **6** with 4-cyanomethylbenzoic acid **9** provided stilbene **10*Z***. Its complex with tris(imidazoline) **13** dissolved in chloroform at concentrations of ⩽8 mg cm^{-3} at ambient temperature. Encouraged by a report by Feast on high photoluminescence

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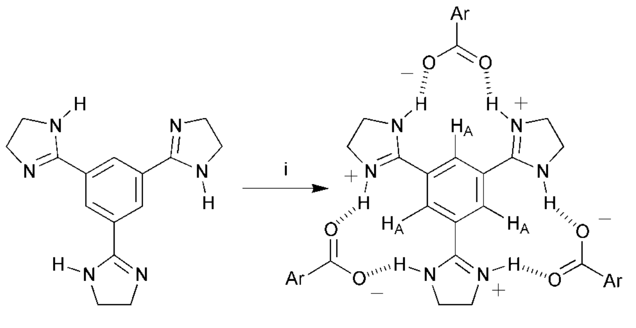
‡Crystallisations were carried out on a scale of preferably about 200–300 mg.



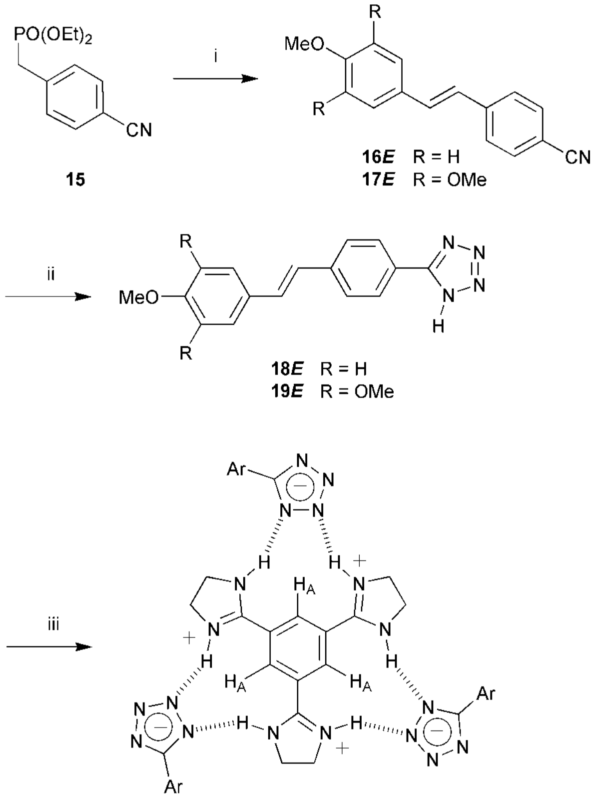
13

14	Ar-CO$_2$H	**14**	Ar-CO$_2$H
a	3*E*	e	12
b	8*E*	f	23
c	10*Z*	g	24
d	11		

Scheme 2 *Reagents and conditions*: i, ArCO$_2$H (3 equiv.), EtOH–CHCl$_3$, reflux.

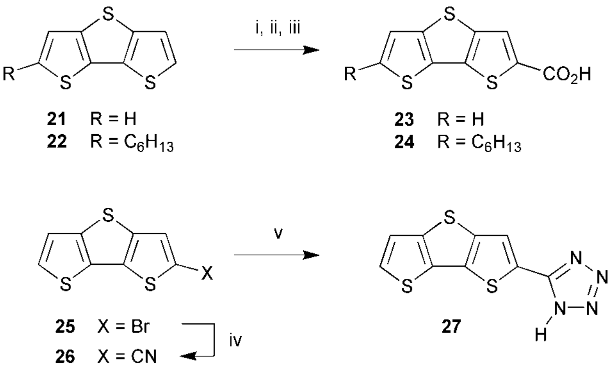
efficiency of tetraphenylethylene derivatives,[16] triphenylacrylic acid derivative **12** with a carboxylic acid group on the vinyl group was then prepared by Perkin condensation of fluoren-9-one with phenylacetic acid.

In addition to these carboxylic acids we synthesised two tetrazolylstilbenes and their corresponding complexes with **13**. Nitriles **16*E*** and **17*E*** were obtained by a Wittig–Horner reaction starting from 4-methoxybenzaldehyde **2** or 3,4,5-trimethoxybenzaldehyde **6**, respectively (Scheme 3). Cycloaddition of ammonium azide[17] gave the corresponding tetrazoles **18*E*** and **19*E*** in medium yields. Purification by column chromatography became necessary to separate the tetrazole component from unreacted starting material. In all cases the *trans* isomer was isolated as long as care was taken to avoid conditions that might lead to photochemical isomerisation. Complexation of tetrazoles was conducted analogously to the stilbenecarboxylic acids.



20	tetrazole
a	18*E*
b	19*E*
c	27

Scheme 3 *Reagents and conditions*: i, **2** or **6**, NaH or Bu^{t}OK, THF (DMF), reflux, 3 h; ii, NaN$_3$, NH$_4$Cl, NMP, 100 °C, 4 h, then HCl; iii, **13** (0.33 equiv.), EtOH–CHCl$_3$, reflux.



Scheme 4 *Reagents and conditions*: i, *n*BuLi, THF, −78 °C to 20 °C, 1 h; ii, CO$_2$, −40 °C; iii, HCl; iv, CuCN, NMP, 150 °C; v, NaN$_3$, NH$_4$Cl, NMP, 100 °C, 4 h, then HCl.

Dithieno[3,2-*b*:2′,3′-*d*]thiophene **21** was readily synthesised from 3-bromothiophene in 4 steps as described previously.[5,18] The 2-alkylated derivative **22** was derived by Friedel–Crafts acylation with hexanoyl chloride, followed by reduction of the keto group with lithium aluminium hydride in the presence of anhydrous AlCl$_3$. Lithiation[6] of **21**,**22** with *n*-butyllithium in THF at −78 °C and subsequent reaction with carbon dioxide gave the carboxylic acids **23**,**24** in good yields (Scheme 4). Cocrystallisation with tris(imidazoline) **13** provided complexes **14f**,**g** of which the hexyl derivative was soluble in chloroform.§ The introduction of a tetrazole group was achieved in 3 steps starting from dithieno[3,2-*b*:2′,3′-*d*]thiophene **21**. Electrophilic bromination introduced a bromo group at the 2-position of the fused thiophene. Treatment with copper(I) cyanide in hot *N*-methylpyrrolidone (NMP) gave the corresponding nitrile **26**, which was then converted to the tetrazole **27** with a mixture of sodium azide and ammonium chloride in NMP. However, overall yields were rather low, partly because of the temperature sensitivity of the dithienothiophene system and partly as a result of the reduced reactivity of the electron-rich nitrile towards cycloaddition with azide anions.

Crystal structure of 14b and 14f

Slow crystallisation of complex **14b** from a solution in CHCl$_3$–EtOH–MeOH gave microcrystals of sufficient quality for X-ray diffractometry which, owing to the small size of the crystals, were examined using the high intensity of a synchrotron radiation source. Microcrystals of complex **14f**, obtained by slow evaporation from EtOH–CHCl$_3$, were analysed likewise using the Daresbury synchrotron radiation microcrystal diffraction facility (station 9.8). Fig. 1a depicts the crystal structure of complex **14b** which crystallised together with molecules of ethanol and water. The crystal structure of complex **14f** (including ethanol and chloroform) is shown in Fig. 2a.

As the two crystal structures exhibit a number of similarities, we will concentrate our initial discussion on complex **14b**. The tris(imidazoline) core is relatively flat, with torsion angles of only 2.4 to 13.3° between the heterocyclic NCN amidinium groups and the central benzene ring. Shortened and almost equal C–O (1.25 Å on average) and C–N bond lengths (1.32 Å

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§All dithienothiophene derivatives proved sensitive to residual HCl in chloroform and crystallisation of the complexes was therefore conducted preferably from EtOH–CH$_2$Cl$_2$ mixtures.

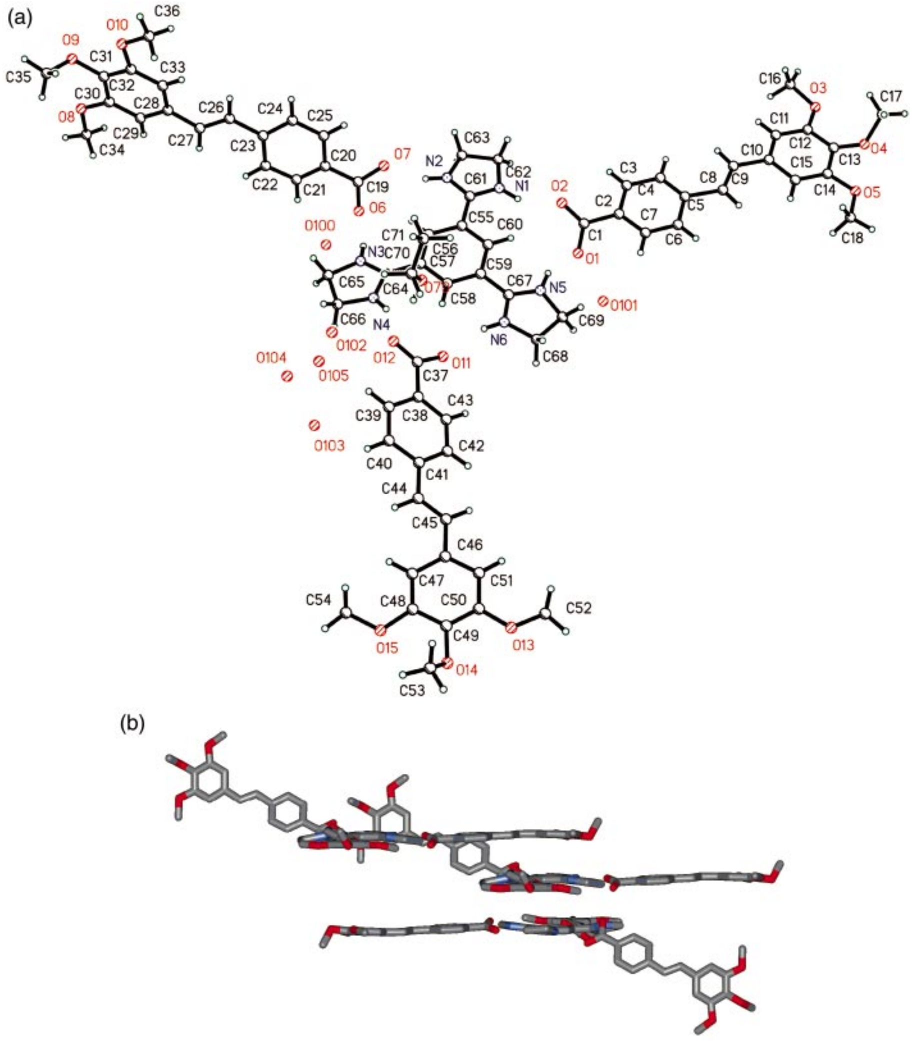


Fig. 1 (*a*) Crystal structure of **14b**, (*b*) side view (hydrogen atoms and included solvent molecules are omitted for clarity).

on average) are consistent with partial double bonds, indicating that proton transfer has occurred from the carboxylic acids to the imidazoline base. All three carboxylate ligands are hydrogen-bonded to the tris(imidazoline) core molecule. Each carboxylate binds in a η^2-like fashion through hydrogen bonds between its carboxylate-O atoms and two NH units belonging to a pair of *meta*-positioned imidazolinium groups. An average N···O distance of 2.68 Å (N–*H*···*O* distance 1.85 Å) and an average N–*H*···*O* angle of 157° is consistent with strong hydrogen bonding. The size of the carboxylate group is slightly too large in comparison to the interstice between two imidazolines which, together with a preference of H-bonds to be linear, accounts for the tilting of the imidazoline substituents and a non-symmetrical binding of the three ligands.

In addition, there are noteworthy close contacts between carboxylate-O atoms and nearby aromatic protons H56A, H58A and H60A. These O···H distances are 2.65 Å on average, but three are considerably smaller than 2.7 Å, the sum of the van der Waals radii. Such short distances [O11···H58A 2.26, O6···H56A 2.53, O7···H56A 2.54, O11···C58 3.19, O6···C56 3.41, O7···C56 3.41 Å] and an average C–H···O angle of 162° fall within the confines of weak directional CH···O hydrogen bonds.[19]

The three methoxy substituents on the stilbene residues adopt a conformation similar to that in mescaline hydrobromide and many of its analogues.[20] Whereas the two outer MeO groups are almost coplanar with the adjacent benzene ring (average torsion angle 7°), the methoxy substituent in the centre twists out of the plane of the benzene ring with a torsion angle of around 76°.

Torsion angles of 3.1, 19.1 and 24.8° are found between the two benzene rings of the stilbenes. Despite all these deviations from planarity the molecule as a whole is still quite flat when viewed from the side (Fig. 1b). Two molecules of complex **14b** lie off-set to each other with an inversion centre in between. The sliding distance between such a pair is 12.34 Å, and the closest distances between atoms in two molecules are 3.22 (N6···C42*), 3.40 (N1···C49*) and 3.45 Å (C61···C50*). Perpendicular to this dimer lies another molecule of the same symmetry and, with a sliding distance of 14.61 Å, only slightly farther away. The closest contacts to this stilbene complex are 3.38 (C60···C14*), 3.42 (C56···C10*) and 3.49 Å (C64···C8*).

Complex **14f** displays a slightly higher degree of order in the crystal packing. Two tris(imidazoline) molecules stack face-to-face with an off-set of 1.4 Å and rotated by 60° relative to each other (Fig. 2b). The dithienothiophenecarboxylate ligands assemble around the two tris(imidazoline)s, forming a centrosymmetric dimer. Although only the benzene rings of two adjacent tris(imidazoline) molecules are completely coplanar, such an arrangement allows oppositely charged ions of adjacent complexes to salt-pack. The closest distances between C atoms in such a dimer are 3.46 (C2···C43*) and 3.48 Å (C6···C4*, C4···C6*). The sliding distance between two nearest pairs is 9.90 Å. The packing diagram of **14f** is shown in Fig. 2c. A more ordered supramolecular packing was so far only observed in complexes of **13** with a tetrazole as ligand in which the smaller tetrazolate anion hydrogen bonded through

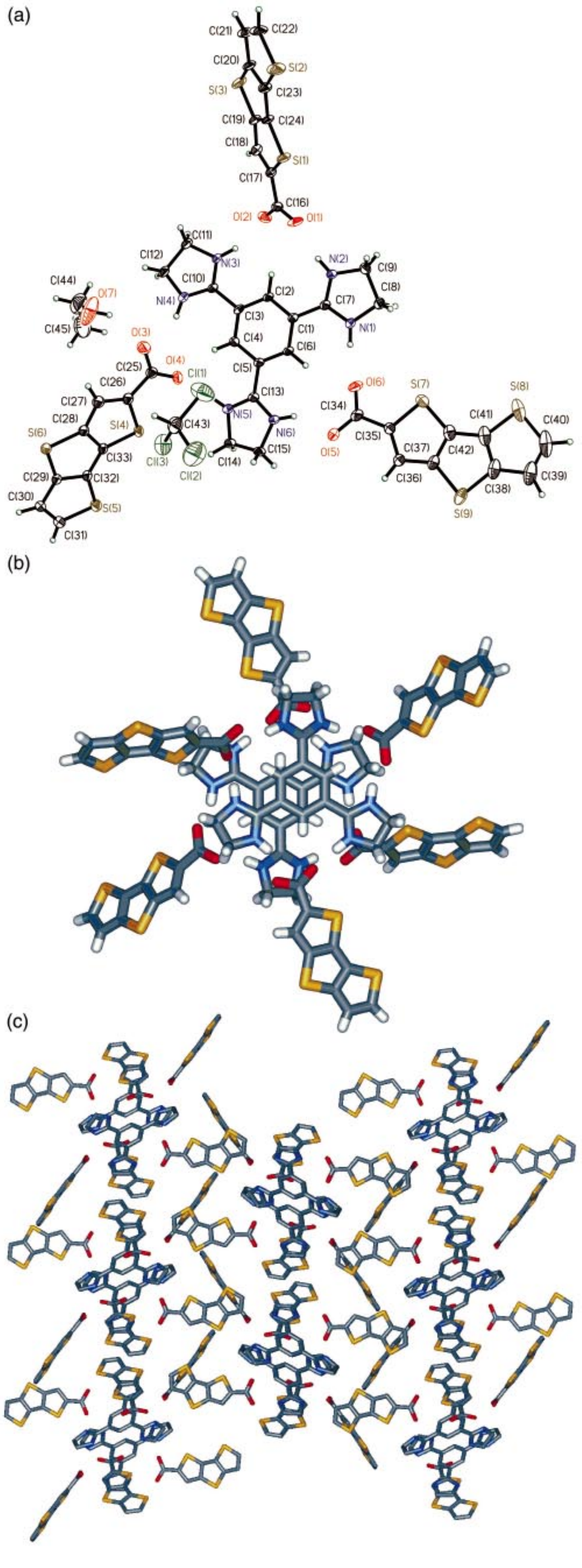


Fig. 2 (*a*) Crystal structure of **14f**, (*b*) top view of two adjacent molecules and (*c*) packing view (hydrogen atoms and included solvent molecules are omitted for clarity).

its N^1 and N^2 atoms and formed a completely planar complex because of the ligand's smaller size.[14] Although columnar packing should be more favourable with tetrazolylstilbenes as ligands, we did not obtain good quality crystals from any of the tetrazole complexes **20a–c** prepared in this study.

We have recently been able to show that complexes of **13** with long chain alkoxy-substituted benzoic acids give rise to columnar mesophase formation.[21] In this respect, both crystal structures present an interesting view about the packing arrangement of typical **13**-carboxylic acid complexes. The almost disk-like shape and the close contacts between adjacent molecules shed some light on the structural forces of how mesogens could be expected to stack into a columnar arrangement. It should, however, be kept in mind that long side chain substituents also influence the structural assembly of the complexes.

Properties of complexes

All carboxylic acid complexes became malleable at elevated temperatures before they formed an isotropic liquid. Although no identifiable liquid crystalline mesophases were observed, several compounds, in particular the hexyl-substituted **14g**, showed distinct crystal–crystal phase transitions in differential scanning calorimetry (DSC) studies instead. The tetrazole and the dithienothiophene complexes were thermally sensitive and decomposed rapidly upon prolonged heating at around the isotropisation temperature.

Complex formation in solution was observed in non-polar solvents only. The ^{1}H NMR spectra of all $CDCl_3$-soluble complexes displayed a distinct signal for the H_A protons (see Scheme 2) on the central benzene ring at $\delta_H \approx 10.1$ that is diagnostic of complexation.[13] There are, in principle, two possible explanations for this unusual chemical shift of an aromatic proton NMR signal. First, additional electric dipole fields are induced by the carboxylate–imidazolinium ion pairs as a result of complexation. Second, both crystal structures indicate that close CH···O contacts exist between the aromatic H_A protons and the surrounding carboxylate ligands, thus providing another cause for the downfield shift of the H_A NMR signal.[22] Only complex **20b** showed signs of weak self-association in chloroform at concentrations above 10^{-3} M, which was a consequence of the known planarised structure of tetrazole complexes.[14] Despite this, the complex had a solubility in chloroform of up to 30 mg cm^{-3}.

Sublimation provided a practical method for depositing various complexes (**14a**, **14b** and **20a**) onto a glass substrate. For example, tetrazolylstilbene complex **20a**, which could not be processed from chloroform, sublimed at 205 °C/ 3×10^{-5} mbar and gave a fine yellow powder with a weak yellow fluorescence. Even in a gradient sublimer the two components of the complex did not separate into different bands. The ^{1}H NMR and IR spectra of the sublimed material confirmed the identity of the complex. Interestingly, under similar conditions sublimation of a complex of **13** and CF_3CO_2H resulted in decomposition of the complex and loss of the volatile acid component. We assume that in certain cases, when both **13** and the acid have comparable sublimation and deposition temperatures, separation under high vacuum can be precluded.

Photoluminescence and electroluminescence studies

Stilbenes **11** and **12**, as well as their corresponding complexes with **13**, lacked fluorescence and were not pursued any further. All other stilbenecarboxylic acids and tetrazolylstilbenes exhibited a strong blue fluorescence in solution that was retained in the complexes with tris(imidazoline) base **13**. An absorption maximum was observed at approx. 335 nm, whereas the photoluminescence maximum varied between 416 and 494 nm. As expected, the introduction of a cyano substituent on the vinylene linker (**10*Z***) gave the compound a blue–green fluorescence in addition to a distinct shift of the photoluminescence maximum to longer wavelengths (494 nm). Surprisingly, there was no significant difference between

Table 1 Absorption and photoluminescence data in dry CH_2Cl_2 (unless otherwise indicated)

Compound	Absorption peak wavelength/nm	PL peak wavelength /nm
3*E*	332[a]	416[a]
Complex **14a**	332	425
8*E*	338	460
Complex **14b**	334[b]	449[b]
10*Z*	338	494
Complex **14c**	334	463
19*E*	336	446
Complex **20b**	338	445
23	314[a]	384[a]
Complex **14f**	318	382
24	334[a]	407[a]
Complex **14g**	326	398

[a]The UV and PL measurements were carried out in CH_2Cl_2–EtOH (1 : 1). [b]UV and PL measurements in $CHCl_3$.

carboxylic acids and tetrazoles and their corresponding complexes (Table 1). The dithienothiophene derivatives had an absorption maximum at around 324 nm and a fluorescence maximum between 385 and 407 nm.

The fluorescent stilbene derivatives, whether in the form of the free acid or as complex with **13**, were sensitive to photochemical isomerisation. Especially in solution the conversion from pure *trans* material to an isomeric mixture containing predominantly the (*Z*)-stilbene proceeded in a couple of hours upon standing in direct sunlight. The *cis* isomers were easily identified by ^1H NMR spectroscopy since both the olefinic and the aromatic *ortho* protons were observed up-field by $\Delta\delta \approx 0.1$–1 relative to the corresponding signals of the *trans* derivatives. Compounds **8*E*** and **10*Z*** were particularly prone to exposure to sunlight, and irradiation rapidly produced isomeric ratios of up to 80 : 20 for **8*Z*** : **8*E***. Similar values were found for the corresponding complexes.

The stilbene complex **14b** is the material of most interest in terms of processability and fluorescence intensity (Fig. 3). The relative fluorescence quantum yield was 8% in solution (measured for a 1×10^{-4} M solution in degassed chloroform, 25 °C, excitation wavelength: 348 nm) in comparison with a quinine sulfate solution (5×10^{-5} M in 0.5 M aqueous H_2SO_4, 25 °C) as a standard (fluorescence quantum yield of 54.6%). A uniform solid film (40 nm in thickness) of complex **14b** was obtained by spin-coating (1600 rpm, 30 s) from a 10 mg cm^{-3} solution in chloroform; however, fluorescence intensity in the solid state was very weak (below 1%) and insufficient for a practical electroluminescent device.

Unlike complex **14b**, complex **20a** was not processable by spin-coating but amenable to vacuum deposition instead. A uniform film with a weak yellow fluorescence was obtained by thermal vapour deposition. Complex **20a** was then tested as an emitting material in an electroluminescent device, where it was sandwiched between a hole-transport and an electron-transport layer as described below. For this, an indium–tin oxide (ITO) coated glass substrate was patterned in stripes (3 mm in width) and washed with water, acetone and ethanol. A hole-transport material, *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenyl[1,1′-biphenyl]-4,4′-diamine (TPD), was deposited on the substrate first. Next, complex **20a** was deposited on top of the TPD layer, followed by an electron-transport material, tris(quinolin-8-olato)aluminium (Alq_3). A cathode metal, magnesium–indium (9 : 1) alloy, was deposited on the organic layers through a shadow mask (2 mm stripes), providing pixels of the size 3 mm × 2 mm each. The device was finally encapsulated to keep out moisture. All depositions were carried out under high vacuum (1×10^{-5} mbar). The structure and thickness of the layers were as follows: ITO (190 nm)/TPD (40 nm)/complex **20a** (40 nm)/Alq_3 (40 nm)/Mg–In (200 nm). The device was examined by applying a dc bias (0 to 30 V) to the electrodes. No visible emission was observed from the device with complex **20a**, whereas a device without the complex showed green electroluminescence from Alq_3. The quenching of fluorescence in the solid state is therefore considered to be a major problem in obtaining electroluminescence from the stilbene complexes.

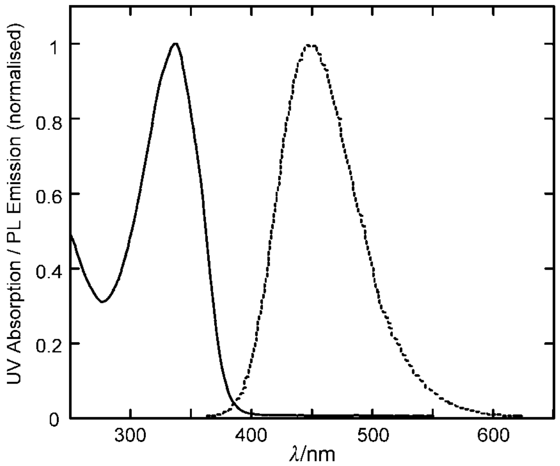
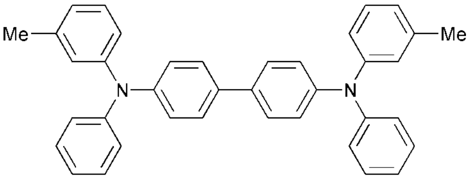
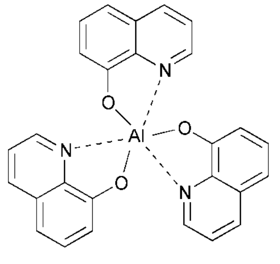


Fig. 3 Absorption (———) and photoluminescence (- - - - -) spectrum of complex **14b** in $CHCl_3$.

As for the dithienothiophene complex, **14g** is processable by spin-coating. A uniform film (40 nm in thickness) was obtained from a 10 mg cm^{-3} solution in chloroform by spin-coating (1600 rpm, 30 s). The compound was applied as a hole-transporting material in an electroluminescent device, since dithienothiophene is considered to be a hole-transport unit.[5] The device [ITO (190 nm)/complex **14g** (40 nm)/TPD (40 nm)/Alq_3 (40 nm)/Ca (50 nm)/Al (150 nm)] was examined by applying a dc bias to the electrodes, but no visible emission could be observed. The device allowed a small current of 0.08 mA cm^{-2} at 15 V, which means that there were not enough carriers injected into the device for light emission. It was concluded that complex **14g** does not have a sufficiently high hole mobility or a suitable HOMO level, probably because the dithienothiophene units in the complex are not conjugated with each other.



TPD



Alq_3

Conclusion

We have described the preparation and optical properties of a number of stilbenecarboxylic acids, tetrazolylstilbenes and dithieno[3,2-*b*:2′,3′-*d*]thiophene-2-carboxylic acids. These acids form non-covalent complexes with tris(imidazoline) base **13** that can be readily purified and isolated by recrystallisation. The introduction of methoxy or hexyl substituents produced complexes with solubility in chloroform large enough for spin-coating. In other cases, sublimation proved an alternative method for the formation of smooth thin films. As long as the electron-withdrawing acid group was attached to the aromatic ring (and not to the vinylene group) the stilbenes and dithienothiophenes and their complexes with **13** showed strong blue fluorescence in solution, whereas in the solid photoluminescence turned out to be in part quenched. When complex **20a** was examined as a light-emitting material in an electroluminescent device, there was unfortunately not enough current allowed in the devices (to exhibit light emission) possibly due to a large band gap, a high carrier injection barrier and a small carrier mobility. A device with a thin film of dithienothiophene complex **14g** as hole-transport layer and Alq_3 as light-emitting material similarly failed to show any light output.

Two crystal structures illustrated that the complexes have an overall disk-shaped structure. The dithienothiophene-containing complex **14f** gave an example of a stacking arrangement that is influenced by salt-packing, with comparatively slight off-sets between molecules along the packing axis. Although the reduced π-overlap between the molecules in the crystal may have been detrimental for charge transport, it nevertheless outlined that more ordered supramolecular structures (at least in the crystal) are accessible in principle. A promising step in this direction has been our recent report on thermotropic liquid-crystalline complexes based on complexes of **13** in which the use of benzoic acid derivates with two or three dodecyloxy substituents induced the formation of columnar mesophases.[21] We anticipate that the judicious choice of binding group (*viz.*, tetrazoles) and substituents could provide an even better and alternative way towards ordered supramolecular assemblies by vapour deposition, solution- or melt-processing.

Experimental

General

All solvents were distilled prior to use. Melting points: Olympus BH-2 polarisation microscope with Linkam TMS91 programmable sample heater. DSC: Mettler TC 11 with TA 4000 Processor. NMR: Bruker AC200, WM-250, DPX-250, DRX 500. TMS was used as standard in the NMR measurements. Multiplicities of ^{13}C signals were determined by DEPT experiments. IR: Bruker Vector 22 FT-IR. UV-Vis: HP 8452A. EI-MS: Varian MAT 311 A (70 eV), MAT 8200 (Hi-Res). CI-MS: Finnigan INCOS 50. High resolution electron impact mass spectra were recorded by the EPSRC Mass Spectrometry Service in Swansea. X-Ray diffraction measurements and crystallographic analysis were made on Station 9.8 at the EPSRC Synchrotron Radiation Source Laboratory in Daresbury. TLC: Aluminium sheets with silica gel $60F_{254}$ (Merck). Chromatography: ICN silica gel 32–63 (ICN Biomedicals) or Merck Kieselgel 60 (230–400 mesh). Elemental analyses: Pharmazeutisches Institut der Heinrich-Heine-Universität Düsseldorf, University Chemical Laboratory Microanalytical Department. Tris(imidazoline) base **13** was prepared as described elsewhere and purified by gradient sublimation at 290 °C/10^{-4} mbar.[23] Tetrahydrofuran (THF) was dried from potassium in a recycling still, using benzophenone ketyl as an indicator. All other solvents were distilled prior to use.

(*E*)-4-[2-(3,4,5-Trimethoxyphenyl)vinyl]benzoic acid 8*E*

To a mixture of ^{t}BuOK (2.47 g, 22 mmol) in THF (8 cm^3) was added a solution of **5**[24] (2.72 g, 10.0 mmol) in THF (4 cm^3), followed by a solution of **6** (1.96 g, 10.0 mmol) in THF (6 cm^3). The red–brown mixture was stirred for 24 h at room temperature before it was acidified with concd. HCl and extracted with $CHCl_3$. After concentrating in vacuum, the residual solid was purified by column chromatography (CH_2Cl_2–Et_2O, 19 : 1 and CH_2Cl_2–MeOH, 10 : 1). The ester **7*E*** (1.32 g) was then combined with KOH (2.00 g, 35.7 mmol) in ethanol (75 cm^3) and refluxed for 3 h. The solution was allowed to cool to room temperature and acidified with concd. HCl. The resulting precipitate was collected by suction filtration, dried and purified by chromatography (CH_2Cl_2–Et_2O, 19 : 1 and CH_2Cl_2–MeOH, 10 : 1) to give **8*E*** as a pale yellow solid (620 mg, 20%), mp 223–226 °C (Found: C, 68.6; H, 5.75. $C_{18}H_{18}O_5$ requires C, 68.8; H, 5.8%); ν_{max} (KBr, cm^{-1}) 1683, 1605, 1581, 1505, 1422, 1316, 1292, 1127; δ_H(200 MHz, $CDCl_3$) 3.88 (3 H, s, OCH_3), 3.92 (6 H, s, OCH_3), 6.76 (2 H, s, ArH), 7.02 (1 H, AB, *J* 16.0, =CH), 7.15 (1 H, AB, *J* 16.0, =CH), 7.56, 8.07 (2 × 2 H, AA′XX′, ArH); δ_C(125 MHz, $CDCl_3$) 56.2, 61.0, 104.0, 126.3, 126.9, 130.7, 131.5 (CH, OCH_3), 128.3, 132.4, 138.6, 142.4, 153.5, 171.9; *m/z* (CI, NH_3) 349 ($M+NH_3+NH_4^+$, 26%), 333, 332 ($M+NH_4^+$, 25, 100), 315 ($M+H^+$, 78); R_f(CH_2Cl_2–MeOH, 9 : 1) 0.69. After a solution of the NMR sample was left standing in the sunlight, additional signals could be detected and were assigned to **8*Z***: δ_H(200 MHz, $CDCl_3$) 3.65 (6 H, s, OCH_3), 3.84 (3 H, s, OCH_3), 6.44 (2 H, s, ArH), 6.58 (1 H, AB, *J* 12.0, =CH), 6.63 (1 H, AB, *J* 12.0, =CH), 7.38, 7.99 (2 × 2 H, AA′XX′, ArH).

(*E*)-4-[2-(3,4,5-Trimethoxyphenyl)vinyl]benzonitrile 17*E*

A solution of **15**[25] (1.41 g, 5.60 mmol) in dry THF (10 cm^3) was added to a KOBu^t (0.673 g, 6.00 mmol) and dry THF (10 cm^3). The solution was stirred for 10 min at room temperature. Then a solution of **6** (1.10 g, 5.60 mmol) in THF (10 cm^3) was added dropwise and stirred for 2 h before the solvent was removed in vacuum and the residue was dissolved in $CHCl_3$ and washed with water (3 × 50 cm^3). The organic extract was dried (Na_2SO_4), concentrated in vacuum, dried and further purified by column chromatography (CH_2Cl_2, then CH_2Cl_2–MeOH, 5 : 1). Yield: 1.27 g (77%), colourless solid, mp 159–162 °C (Found: C, 72.4; H, 5.5; N, 4.5. $C_{18}H_{17}NO_3$ requires C, 73.2; H, 5.8; N, 4.7%); ν_{max} (KBr, cm^{-1}) 2219 (CN), 1599, 1582, 1509, 1459, 1421, 1137, 1003, 839; δ_H(500 MHz, $CDCl_3$) 3.88 (3 H, s, OCH_3), 3.92 (6 H, s, OCH_3), 6.76 (2 H, s, ArH), 6.98 (1 H, AB, *J* 16.4, =CH), 7.14 (1 H, AB, *J* 16.4, =CH), 7.57, 7.63 (2 × 2 H, AA′XX′, ArH); δ_C(125 MHz, $CDCl_3$) 56.2, 61.0, 104.2, 126.2, 126.8, 132.4, 132.5 (CH, CH_3), 110.5, 119.0, 132.0, 138.9, 141.8, 153.5 (*ipso*-C, CN); *m/z* (CI, NH_3) 330 ($M+NH_3+NH_4^+$, 17%), 315, 313 ($M+NH_4^+$, 77, 100), 296 ($M+H^+$, 6); R_f(CH_2Cl_2) 0.37.

(*E*)-5-{4-[2-(3,4,5-Trimethoxyphenyl)vinyl]phenyl}-1*H*-tetrazole 19*E*

Nitrile **17*E*** (0.94 g, 3.20 mmol), NaN_3 (0.46, 7.00 mmol) and NH_4Cl (0.38 g, 7.00 mmol) in NMP (15 cm^3) were heated to 100 °C for 48 h. The reaction mixture was added dropwise to H_2O (200 cm^3)–concd. HCl (20 cm^3). The precipitate was collected by suction filtration, dried, and purified by column chromatography (CH_2Cl_2 and CH_2Cl_2–MeOH, 5 : 1). Yield: 0.29 g (26%), pale yellow platelets, mp 172–179 °C (Found: C, 63.6; H, 5.3; N, 16.7. $C_{18}H_{18}N_4O_3$ requires C, 63.9; H, 5.4; N, 16.6%); ν_{max} (KBr, cm^{-1}) 1611, 1583, 1508, 1125; δ_H(500 MHz, [$^2H_6$]DMSO) 3.70 (3 H, s, OCH_3), 3.86 (6 H, s, OCH_3), 6.99 (2 H, s, ArH), 7.32 (1 H, AB, *J* 16.4, =CH), 7.37 (1 H, AB, *J* 16.4, =CH), 7.82, 8.06 (2 × 2 H, AA′XX′, ArH); δ_C(125 MHz, [$^2H_6$]DMSO) 55.8, 60.0, 104.1, 126.6, 127.0, 127.3, 130.6 (CH, CH_3), 132.3, 137.6, 140.0, 153.0 (*ipso*-C, C=N); *m/z* (CI, NH_3) 373 ($M+NH_3+NH_4^+$, 26%), 357, 356 ($M+NH_4^+$, 15, 100), 340, 339 ($M+H^+$, 12, 95); R_f(CH_2Cl_2–MeOH, 4 : 1) 0.50.

Dithieno[3,2-*b*:2′,3′-*d*]thiophene-2-carboxylic acid 23

The compound was prepared by a modified literature procedure.[26] *n*-Butyllithium (1.6 M in hexane, 1.18 cm^3, 1.88 mmol) was added dropwise to a solution of **21**[5,18] (368 mg, 1.88 mmol) in THF (4 cm^3) at −78 °C under N_2. The solution turned cloudy green within 10 min and was allowed to warm up to room temperature. After 40 min, it was cooled to approx. −40 °C. The cold solution was then transferred to a syringe and added dropwise to dry ice in a flask kept under N_2. After warming up to room temperature, water (30 cm^3) and ether (40 cm^3) were added. The organic layer was separated and discarded. The aqueous layer was acidified with HCl (10 M, 10 cm^3). The yellow solid was collected by suction filtration and recrystallised from 33% acetic acid to give **23** as a fine yellow green powder (286 mg, 61%), mp 276 °C (compound sublimed, lit.[26] 275–277 °C); ν_{max} (KBr, cm^{-1}) 3090, 3823, 2559, 1652, 1504, 1428, 1311, 1265, 1164, 928, 750, 716, 602; δ_H(250 MHz, $CDCl_3$) 7.31 (1 H, d, *J* 5.1), 7.56 (2 H, d, *J* 5.1), 7.94 (1 H, s).

2-Hexyldithieno[3,2-*b*:2′,3′-*d*]thiophene 22

To a stirred solution of **21**[5] (339 mg, 1.73 mmol) in dry CH_2Cl_2 (50 cm^3) was added hexanoyl chloride (0.25 cm^3, 1.79 mmol). The mixture was stirred for 0.5 h at room temperature, cooled to 0 °C, and $AlCl_3$ (267 mg, 2.0 mmol) was added portionwise. The mixture was then allowed to warm to 25 °C and stirred for 18 h. The reaction was quenched by the addition of water (30 cm^3) and acidified with 2 M aqueous HCl (50 cm^3). The mixture was extracted with CH_2Cl_2 (2 × 20 cm^3). The organic layers were combined, washed with water (30 cm^3), dried ($MgSO_4$) and concentrated in vacuum. Column chromatography (hexane–CH_2Cl_2, 1 : 1) afforded 1-(dithieno[3,2-*b*:2′,3′-*d*]thiophen-2-yl)hexan-1-one (355 mg, 70%) as a colourless solid, mp 140–141 °C (Found: C, 57.0; H, 4.8. $C_{14}H_{14}S_3O$ requires C, 57.1; H, 4.8%); ν_{max} (KBr, cm^{-1}) 2923, 2864, 1641, 1490, 1362, 1209, 703; δ_H(250 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.5, CH_3), 1.25 (4 H, br s, CH_2), 1.78 (2 H, m, CH_2), 2.93 (2 H, t, *J* 7.5, CH_2CO), 7.32 (1 H, d, *J* 5.2), 7.52 (1 H, d, *J* 5.2), 7.91 (1 H, s, ArH); δ_C(100 MHz, $CDCl_3$) 13.9, 22.5, 24.7, 31.6, 39.0, 120.9, 125.5, 129.0, 130.9, 136.9, 141.2, 144.4, 144.9, 193.7; *m*/*z* (EI) 294 (M^+, 28%), 238 (35), 223 (20), 195 (14), 175 (10), 163 (12), 151 (16), 123 (35), 83 (100); R_f(hexane–CH_2Cl_2, 1 : 1) 0.3. Anhydrous ether (6 cm^3) at 0 °C was added to separate batches of $LiAlH_4$ (160 mg, 4.2 mmol) and $AlCl_3$ (133 mg, 1.0 mmol), and the resulting mixtures were combined. To this mixture was added 1-(dithieno[3,2-*b*:2′,3′-*d*]thiophen-2-yl)hexan-1-one (127 mg, 0.43 mmol) in dry ether at 0 °C. The mixture was allowed to warm to room temperature and then stirred for 3 h. The reaction was quenched by the careful addition of ether (2 cm^3) and 2 M aqueous HCl (4 cm^3). The product was extracted by washing the gray precipitate with ether (3 × 10 cm^3). The combined organic washings were dried ($MgSO_4$), and the solvent was removed in vacuum. Column chromatography (hexane) afforded **22** (110 mg, 90%) as transparent crystals, mp 52–53 °C (Found: C, 60.0; H, 5.8. $C_{14}H_{16}S_3$ requires C, 60.0; H, 5.8%); ν_{max} ($CDCl_3$, cm^{-1}) 2956, 2930, 2857, 817, 604; δ_H(250 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.5, CH_3), 1.25–1.46 (4 H, m, CH_2), 1.73 (2 H, m, CH_2), 2.90 (2 H, t, *J* 7.0, CH_2), 6.96 (1 H, s), 7.25 (1 H, d, *J* 5.3), 7.27 (1 H, d, *J* 5.3, ArH); δ_C(100 MHz, $CDCl_3$) 14.1, 22.6, 28.0, 30.9, 31.2, 31.6, 117.5, 120.7, 124.9, 128.7, 131.2, 140.1, 140.8, 147.3; *m*/*z* (EI) 281 (M^+, 7%), 211 (19), 209 (100); R_f(hexane) 0.5.

6-Hexyldithieno[3,2-*b*:2′,3′-*d*]thiophene-2-carboxylic acid 24

To a solution of **22** (200 mg, 0.71 mmol) in dry THF (30 cm^3) at −78 °C was added dropwise *n*-butyllithium (0.50 cm^3, 15% in hexane, 0.80 mmol). The reaction mixture was allowed to warm to room temperature and was stirred for 0.5 h. It was then cooled to −30 °C and carbon dioxide (CO_2) gas was bubbled through the solution. The mixture was allowed to warm to room temperature and stirred for 0.5 h before CO_2 gas introduction was stopped. After stirring for further 2 h, the reaction was quenched by addition of water and 2 M aqueous HCl (30 cm^3). The mixture was extracted with ether (3 × 20 cm^3). The combined organic layer was dried ($MgSO_4$), and the solvent was removed in vacuum. Column chromatography (EtOH–ethyl acetate, 1 : 1) gave **24** (210 mg, 90%). Recrystallisation from EtOH–$CHCl_3$ (1 : 1) afforded needle-like crystals, whereas sublimation (150 °C, 10^{-5} mbar, 4 h) afforded a colourless powder, mp 192–193 °C; ν_{max} ($CDCl_3$, cm^{-1}) 2924, 2851, 2552, 1652, 1497, 1420, 1285, 1162, 908, 865, 808, 753, 688; δ_H(250 MHz, $CDCl_3$–CD_3OD) 0.75 (3 H, t, *J* 6.5, CH_3), 1.13–1.29 (6 H, m, CH_2), 1.60 (2 H, m, CH_2CH_2Ar), 2.78 (2 H, t, *J* 7.0, CH_2Ar), 6.88 (1 H, s, ArH), 7.26 (1 H, s, ArH); *m*/*z* (CI, NH_3) 325.0387 (M + H^+. $C_{15}H_{17}O_2S_3$ requires 325.0390).

General procedure for the preparation of the complexes. Carboxylic acid or tetrazole (3 equiv.) and **13** (1 equiv.) were dissolved in hot ethanol (40 cm^3 mmol^{-1}) to which a certain amount of $CHCl_3$ (5–10 cm^3) had to be added as cosolvent. After filtration of the hot solution and concentration, the crude product was crystallised from the solvent (mixture) indicated for each complex.

14b. Yield: 75% (from EtOH–$CHCl_3$), yellow crystals, DSC: K_1/167 (ΔH -30 J g^{-1})/K_2/243 (ΔH 83 J g^{-1})/$I_{decomp.}$ (Found: C, 65.4; H, 6.1; N, 6.6. $C_{69}H_{72}N_6O_{15} \times 2\ H_2O$ requires C, 65.7; H, 6.1; N, 6.7%); λ_{max} ($CHCl_3$) 332 nm (ε 88 000 M^{-1} cm^{-1}); ν_{max} (KBr, cm^{-1}) 1640, 1584, 1538, 1504, 1379, 1124; δ_H(500 MHz, $CDCl_3$) 3.87 (9 H, s, OCH_3), 3.92 (18 H, s, OCH_3), 4.16 (12 H, s, NCH_2), 6.75 (6 H, s, ArH), 7.04 (3 H, AB, *J* 16.0, =CH), 7.10 (3 H, AB, *J* 16.0, =CH), 7.52, 8.07 (2 × 6 H, AA′XX′, ArH), 10.12 (3 H, s, H_A); δ_C(125 MHz, $CDCl_3$, 15.1 mg/0.8 cm^3) 45.5, 56.2, 61.0, 103.8, 125.4, 126.0, 127.7, 129.7, 129.9, 132.9, 134.8, 136.2, 138.2, 139.5, 153.5, 163.1, 173.5. After exposure of an NMR sample to sunlight for several hours, a chloroform solution showed additional ^{1}H NMR signals for the (*Z*) isomer, δ_H(200 MHz, $CDCl_3$) 3.87 (9 H, s, OCH_3), 3.92 (18 H, s, OCH_3), 6.75 (6 H, s, ArH), 7.04 (3 H, AB, *J* 16.0, =CH), 7.10 (3 H, AB, *J* 16.0, =CH), 7.52, 8.07 (2 × 6 H, AA′XX′, ArH).

14f. Yield: 57% (from EtOH–$CHCl_3$), pale yellow crystals, mp 265 °C; λ_{max} ($CHCl_3$–EtOH, 1 : 1) 314 nm; ν_{max} (KBr, cm^{-1}) 2917, 2848, 1644, 1492, 1466, 1362, 1189, 838; δ_H(500 MHz, CD_3OD) 4.04 (12 H, s, NCH_2), 7.38 (3 H, d, *J* 5.1), 7.59 (3 H, d, *J* 5.1), 7.83 (3 H, s, ArH), 8.52 (3 H, s, H_A). Additional signals could be assigned to ethanol and chloroform that were included in crystals **14f**.

14g. Yield: 80% (from MeOH–CH_2Cl_2), colourless crystals, DSC: K_1/114 (ΔH 33 J g^{-1})/K_2/171 (ΔH 2 J g^{-1})/K_3/191 (ΔH 16 J g^{-1})/I (Found: C, 55.5; H, 5.25; N, 6.4. $C_{60}H_{66}N_6O_6S_9 \times 2\ H_2O$ requires C, 55.8; H, 5.5; N, 6.5%); λ_{max} ($CHCl_3$) 322 nm; ν_{max} (KBr, cm^{-1}) 1584, 1499, 1288, 1155; δ_H(500 MHz, $CDCl_3$) 0.89 (9 H, t, *J* 6.9, CH_3), 1.21–1.41 (18 H, m), 1.72 (6 H, m, CH_2), 2.89 (6 H, t, *J* 7.5, CH_2), 4.20 (12 H, s, NCH_2), 6.97 (3 H, s), 7.80 (3 H, s, ArH), 9.94 (3 H, s, H_A), 12.78 (6 H, br s, NH); δ_C(62.5 MHz, $CDCl_3$) 14.1, 22.6, 28.7, 31.2, 31.6, 45.5, 117.6, 123.9, 125.3, 129.0, 134.3, 134.7, 139.4, 142.2, 142.4, 148.6, 162.9, 169.1.

20a. Yield: 77% (from EtOH–$CHCl_3$), yellow crystals, mp 283–284 °C (decomp.) (Found: C, 67.6; H, 5.2; N, 22.65. $C_{63}H_{60}N_{18}O_3$ requires C, 67.7; H, 5.4; N, 22.6%); λ_{max} ($CHCl_3$–MeOH, 24 : 1) 338 nm (ε 65 000 M^{-1} cm^{-1}); ν_{max} (KBr, cm^{-1}) 1647, 1640, 1602, 1577, 1507, 1251, 1176; δ_H(500 MHz,

$CDCl_3$–[$^2H_6$]DMSO, 1 : 1) 3.81 (9 H, s, OCH_3), 3.86 (12 H, br s, NCH_2), 6.92, 7.51 (2 × 6 H, AA′XX′, ArH), 7.05 (3 H, AB, *J* 15.8, =CH), 7.18 (3 H, AB, *J* 15.8, =CH), 7.60, 8.04 (2 × 6 H, AA′XX′, ArH), 8.59 (3 H, s, H_A).

20b. Yield: 60% (from EtOH–$CHCl_3$), yellow crystals, mp 188–190 °C (Found: C, 62.6; H, 5.4; N, 19.2. $C_{69}H_{72}N_{18}O_9 \times H_2O$ requires C, 63.0; H, 5.7; N, 19.2%); λ_{max} ($CHCl_3$) 338 nm (ε 110 000 M^{-1} cm^{-1}); ν_{max} (KBr, cm^{-1}) 1641, 1580, 1505, 1125; δ_H(500 MHz, $CDCl_3$, 10^{-3} M) 3.87 (9 H, s, OCH_3), 3.89 (18 H, s, OCH_3), 4.24 (12 H, s, NCH_2), 6.71 (6 H, s, ArH), 6.92 (3 H, AB, *J* 16.4, =CH), 6.99 (3 H, AB, *J* 16.4, =CH), 7.48, 8.05 (2 × 6 H, AA′XX′, ArH), 9.57 (3 H, s, H_A).

Single-crystal X-ray diffraction of 14b and 14f

Data were collected for **14b** and **14f** at Station 9.8, Daresbury SRS, from microcrystalline needles obtained by slow evaporation of solutions in $CHCl_3$–EtOH–MeOH and $CHCl_3$–EtOH mixtures, respectively. Exposures covered 0.2° in ω and intensities were integrated from several series of exposures.[27] The unit-cell parameters were refined using the program *LSCELL*[28] and the data were corrected for absorption and incident beam decay using the program *SADABS*.[29] The structures were solved by direct methods using *SHELXS*-97[30] and refined against F^2 using *SHELXL*-97.[31] For **14b**, the data do not support anisotropic refinement and all atoms in this structure were refined with an isotropic displacement parameter. The large internal *R*-factor ($R_{int} = 0.1514$) in this case may be indicative of crystal decay in the incident beam or suggest that the microcrystal was not single.

Crystal data for 14b. Empirical formula $C_{70}H_{83}N_6O_{19.5}$; formula weight (*M*) 1320.42; temperature 150(2) K; crystal system monoclinic; space group $P2_1/n$; unit-cell dimensions $a = 14.577(2)$, $b = 22.601(4)$, $c = 22.184(3)$ Å, $\beta = 105.52(3)°$; volume 7042.1(18) Å^3; $Z = 4$; $\lambda = 0.6919$ Å; $\mu = 0.091$ mm^{-1}; reflections collected 27 179; independent reflections 9638 ($R_{int} = 0.1514$); final *R* indices ($I > 2\sigma(I)$) $R1 = 0.1586$, $wR2 = 0.3645$. CCDC reference number 153425. See http://www.rsc.org/suppdata/jm/b0/b009406o/ for crystallographic files in .cif format.

Crystal data for 14f. Empirical formula $C_{45}H_{37}Cl_3N_6O_7S_9$; formula weight (*M*) 1168.70; temperature 150(2) K; crystal system monoclinic; space group $P2_1/c$; unit-cell dimensions $a = 9.8977(7)$, $b = 32.031(2)$, $c = 16.2090(10)$ Å, $\beta = 107.72(1)°$; volume 4895.0(6) Å^3; $Z = 4$; $\lambda = 0.6883$ Å; $\mu = 0.630$ mm^{-1}; reflections collected 33 111; independent reflections 12617 ($R_{int} = 0.0625$); final *R* indices ($I > 2\sigma(I)$) $R1 = 0.0687$, $wR2 = 0.1764$. CCDC reference number 153426. See http://www.rsc.org/suppdata/jm/b0/b009406o/ for crystallographic files in .cif format.

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