

Synthesis, optical properties, crystal structures and phase behaviour of symmetric, conjugated ethynylarene-based rigid rods with terminal carboxylate groups

Tolulope M. Fasina,^{*ab} Jonathan C. Collings,^a Jacqueline M. Burke,^a Andrei S. Batsanov,^a Richard M. Ward,^a David Albesa-Jové,^a Laurent Porrès,^a Andrew Beeby,^a Judith A. K. Howard,^a Andrew J. Scott,^c William Clegg,^c Stephen W. Watt,^{†d} Christopher Viney^{‡d} and Todd B. Marder^{*a}

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Sonogashira cross-coupling reactions of 4-ethynylmethylbenzoate (**1**) with aryl halides gave 1,2-bis(4-carbomethoxyphenyl)ethyne (**2**), 1,4-bis(4-carbomethoxyphenylethynyl)benzene (**3**), 1,4-bis(4-carbomethoxyphenylethynyl)tetrafluorobenzene (**4**) and 9,10-bis(4-carbomethoxyphenylethynyl)anthracene (**5**), protected precursors to conjugated rigid rod bis(carboxylato) ligands. The compound 1,4-bis(4-carbomethoxyphenyl)butadiyne (**6**) was prepared by the oxidative homo-coupling of **1**. The hydrolysis of **2** and **3** by NaOH in methanol gave the sodium salts of the respective carboxylate anions and subsequent treatment with HCl gave the corresponding free carboxylic acids. Compounds **2–6** were characterised by absorption, emission, IR, NMR and mass spectrometry and examined for liquid crystal phase behaviour by differential thermal analysis (DTA) and transmitted polarised light microscopy (TPLM). Compound **4** exhibited a nematic phase stable from 233.6 °C until decomposition at 320 °C. The single-crystal structures of **2**, **5** and **6** were determined by X-ray diffraction at 110–160 K.

Introduction

The molecular assembly of coordination polymers and supramolecules has provided a facile approach to novel molecular materials for applications in catalysis, separations and molecular recognition.¹ Most of the initial research has focused on the use of neutral, rigid *N,N'*-spacers such as 4,4'-bipyridine and extended analogues.² However, the potential applications of many of the resulting structures have been restricted as they either contained interpenetrating networks or have the anion clathrated within the cavities.

The availability of two oxygen atoms and four electron pairs for ligation in carboxylate ligands allows for a variety of coordination modes ranging from monodentate through chelating, bridging and even polydentate binding. This results in the synthesis of polymers having a wider variety of topological arrangements.³ Furthermore, the use of anionic carboxylate ligands results in the formation of neutral metal complexes, which eliminates the problem of counter-ion clathration. Carboxylate chemistry has thus recently allowed the synthesis of robust, porous materials with useful applications.⁴

Benzene polycarboxylic acids, such as 1,2,4,5-benzenetetracarboxylic acid,^{5a} 1,3,5-benzenetricarboxylic acid,^{5b,c} 1,4-benzenedicarboxylic acid,^{5d-f} and the related [(4,4',4''-tricarboxydodecachlorotriphenyl)methyl radical (PTMTC)]^{5g-j} have been used as ligands in the formation of highly porous

metal-organic supramolecular assemblies. Recently, several groups reported the use of extended rod-like carboxylate spacers such as 4,4'-biphenyldicarboxylic acid,⁶ 2,6-naphthalenedicarboxylic acid,⁷ and systems containing fused rings^{1e} in the construction of a variety of 1D, 2D and 3D frameworks with novel topologies. Several phenylene-ethynylene-based rigid rods with terminal carboxylic acid groups have been used in composite materials which incorporate regularly spaced CdS and PbS nanoparticles, by reaction of their cadmium and lead carboxylate salts with H₂S.^{8a,b} In addition, the photoluminescence and lasing properties of thin films of substituted oligo(phenylene-ethynylenes) bearing benzenecarboxylate end groups have been examined,^{8c} and liquid crystal phase behaviour of luminescent bis(phenylethynyl)anthracenes bearing long-chain carboxylate groups have been reported.^{8d}

While most of the carboxylate ligands were used either as sodium salts or as the free acids, it has been shown with unsymmetrical ligands that esters do hydrolyse *in situ* to give the acids when utilized under hydrothermal conditions.⁹ As part of an ongoing programme to examine the properties of rigid rods based on the phenylene-ethynylene motif,^{2h,10} we report herein the synthesis and characterisation of a series of extended bis(carboxymethyl) compounds and their hydrolysed bis(carboxylic acids) containing rigid rod conjugated backbones.

Results and discussion

Owing to the potential reactivity of the acid group under the Sonogashira cross-coupling reaction conditions, the compounds were initially prepared as their methyl esters. This

[†] Present address: Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB1 1EW.

[‡] Present address: School of Engineering, University of California at Merced, P.O. Box 2039, Merced, CA 95344, USA.

*Todd.Marder@durham.ac.uk (Todd B. Marder)

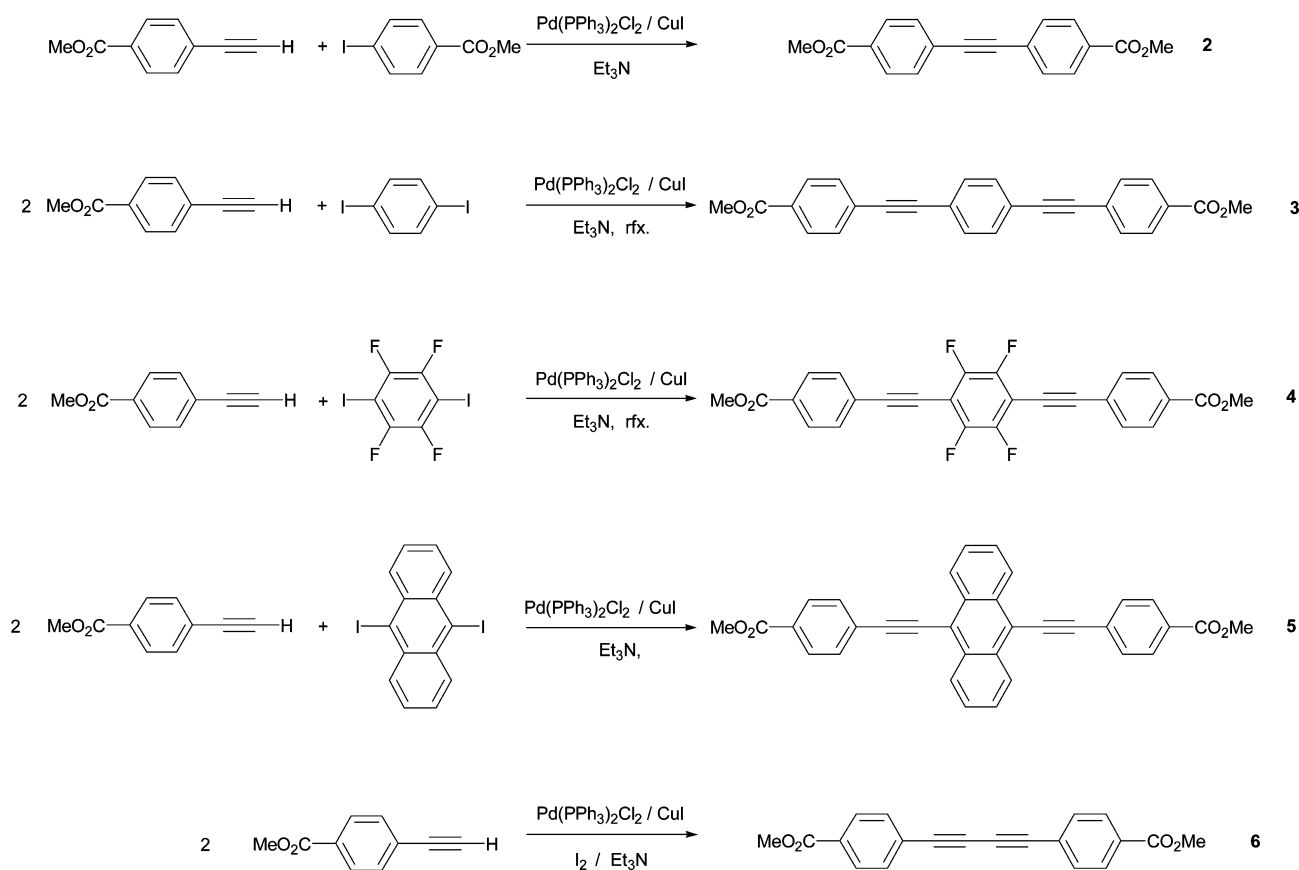
allowed for the isolation of the products in high yield by passage through short silica gel columns with hot toluene, and subsequent crystallisation upon cooling. The terminal alkyne, 4-ethynyl(methylbenzoate) (**1**), used as precursor to the conjugated systems, was prepared by a modification of the literature procedure,¹¹ involving the Sonogashira cross-coupling of trimethylsilylacetylene (TMSA) to 4-iodo(methylbenzoate) at room temperature, followed by hydrodesilylation using sodium carbonate in MeOH.

Compounds **2–5** were synthesised *via* Sonogashira reactions of **1** with the appropriate aryl halide using Pd(PPh₃)₂Cl₂ and CuI in triethylamine,¹² as shown in Scheme 1. Thus, 4-iodo(methylbenzoate) was coupled with **1** at room temperature to give **2** in 91% yield. It was synthesised previously *via* a one-pot coupling reaction involving 4-iodo(methylbenzoate) and TMSA.¹³ Compounds **3** and **4** were prepared in 46 and 96% yields respectively by coupling of two equivalents of **1** to 1,4-diiodobenzene and 1,4-diiodotetrafluorobenzene, respectively. Compound **5** was prepared *via* coupling of two equivalents of **1** to the commercially available 9,10-dibromoanthracene using the more active catalyst system prepared *in situ* from Pd(PhCN)₂Cl₂ and the electron-rich phosphine, P^tBu₃,¹⁴ which allowed the reaction to proceed at room temperature in 80% yield. However, as the product was often contaminated with traces of the mono-coupled material, we chose to utilize samples prepared in similar yield but higher purity from the more reactive 9,10-diiodoanthracene for subsequent studies.

In addition, 1,4-bis(4-carbomethoxyphenyl)butadiyne **6** was obtained in good yields *via* the oxidative homo-coupling of **1** using a stoichiometric amount of iodine in the presence of catalytic Pd(PPh₃)₂Cl₂ and CuI in triethylamine at room temperature.¹⁵ This is also shown in Scheme 1. Compounds **3** and **6** have been previously reported, although no synthetic or characterisation details were given.¹⁶ The esters **2** and **3** were converted to the sodium salts of the corresponding acids *via* reaction with NaOH, which were subsequently converted to the free acids by treatment with HCl to give compounds **7** and **8** respectively.

Optical properties

The optical properties (absorption, fluorescence, quantum yield and lifetime) of all compounds are presented in Table 1. Compounds **2–4** display an intense absorption band in the UV region. These chromophores are also highly fluorescent in the UV, with quantum yields of up to 0.9. Compound **6** displays similar UV absorption and fluorescence properties, but with a defined vibrational substructure in absorption. This chromophore shows a markedly lower quantum yield (1%) and a very short fluorescence lifetime (70 ps), which are consistent with the high non-radiative deactivation processes in diyne derivatives.^{10e} Lastly, compound **5** exhibits absorption and emission in the visible range. Compared with the phenylene derivative **3**, this anthryl chromophore induces a smaller Stokes shift, slightly lower quantum yield, and a fluorescence lifetime reaching 2.7 ns.



Scheme 1

Table 1 Absorption and emission data for compounds **2–6** in acetonitrile, cyclohexane and dichloromethane

Cpd	MeCN						C ₆ H ₁₂						CH ₂ Cl ₂					
	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{cm}^{-1}\text{M}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	Stokes shift/cm ⁻¹	ϕ	τ/ns	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{cm}^{-1}\text{M}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	Stokes shift/cm ⁻¹	ϕ	τ/ns	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{cm}^{-1}\text{M}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	Stokes shift/cm ⁻¹	ϕ	τ/ns
2	304	41 700	330	2600	0.64	0.61	306	^a	328	2200	0.72	0.72	307	45 600	333	2500	0.70	0.64
3	332	^a	364	2650	0.87	0.67	335	^a	362	2200	0.81		335	65 600	367	2600	0.91	0.68
4	331	^a	360	2400	0.85	0.635	335	^a	361	2150	0.85		334	43 500	364	2500	0.86	0.62
5	(446)	^a	483	(1700)		2.74	448	^a	482	1600	0.63	2.51	(451)	58 700	488	(1700)	0.64	2.67
	473		400				(472)		(400)			478		400				
6	322	^a	351	2600	0.006	—	325	^a	352	2400	0.007		326	48 200	355	2500	0.012	0.070

^a Not sufficiently soluble for accurate measurement of the extinction coefficient.

Crystal structures

Compounds **2**, **5** and **6** have been characterised by single-crystal X-ray diffraction (Fig. 1). Molecule **2** has a crystallographic inversion centre. The carboxy group is inclined by only 5.6° to the plane of the benzene ring. The C(9)=C(9') bond is tilted by 4.5° out of the latter plane, hence the two

benzene rings of the molecule are parallel but not coplanar, with an interplanar separation of 0.20 Å. The same distortion was observed in unsubstituted tolan,¹⁷ 4,4'-bis(methylamino-carbonyl)tolan¹⁸ and 4-amino-4'-nitrotoan,¹⁹ the last two molecules also displaying nearly coplanar orientations of the 4,4'-substituents. Molecules of **2** pack in layers parallel to the (001) plane. Within a layer, the long axes of all molecules are

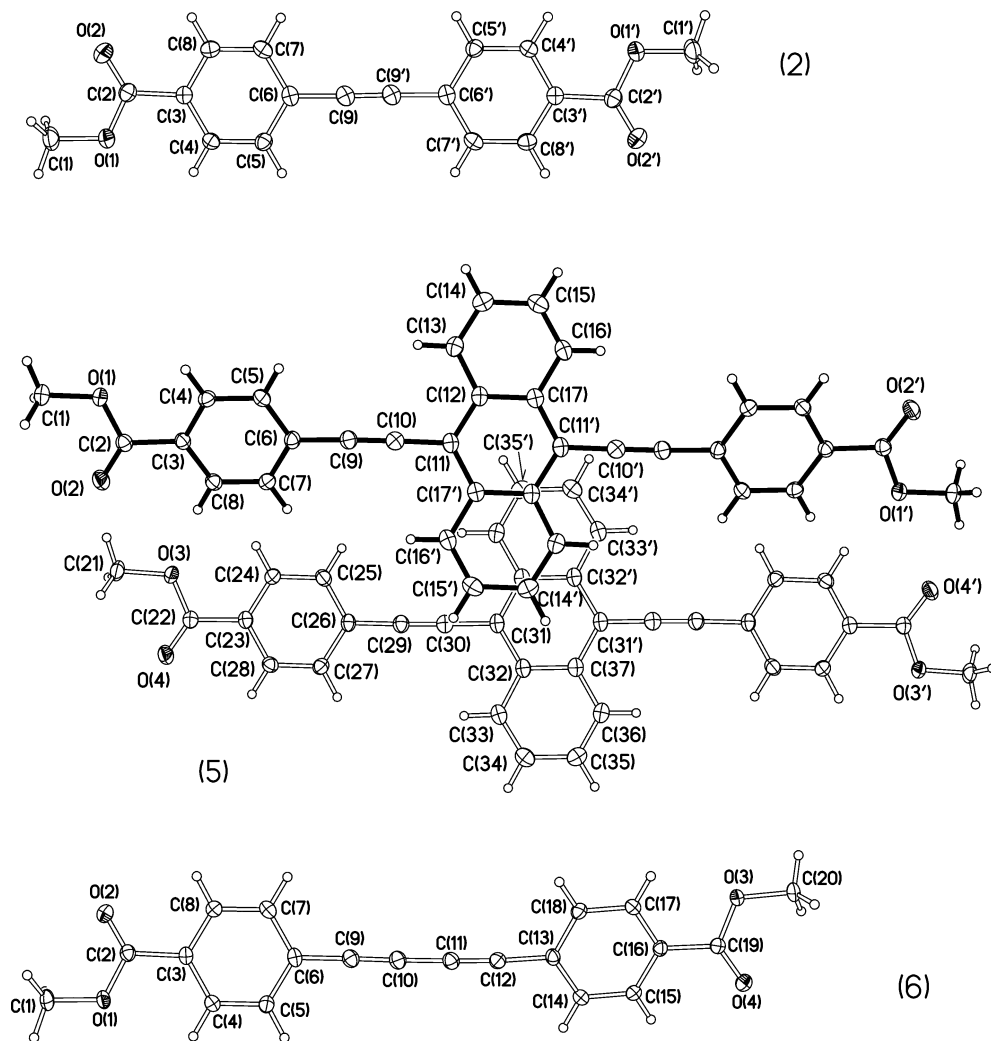


Fig. 1 Molecular structures of **2**, **5** (two independent molecules) and **6**, showing displacement ellipsoids at the 50% probability level. Atoms generated by inversion centres are primed. Selected bond distances (Å) in **2**: C(6)–C(9) 1.433(2), C(9)–C(9') 1.199(3); in **5**: C(6)–C(9) 1.439(2), C(9)–C(10) 1.194(2), C(10)–C(11) 1.430(2), C(26)–C(29) 1.437(2), C(29)–C(30) 1.196(2), C(30)–C(31) 1.429(2); in **6**: C(6)–C(9) 1.432(2), C(9)–C(10) 1.205(2), C(10)–C(11) 1.372(2), C(11)–C(12) 1.204(2), C(12)–C(13) 1.432(2).

parallel and are inclined by 67.5° to the layer plane, while molecular planes contact face-to-edge at a dihedral angle of *ca.* 48° , *i.e.* they form a herringbone motif.

The unit cell of **5** contains two crystallographically independent molecules, both of which lie on inversion centres. The dihedral angle between the benzene and anthracene planes is quite different in the two molecules, being 30.9 and 5.2° , respectively, while the angle between the benzene and carboxy-group planes is similar and small, 8.4 vs. 9.9° , and the C=C bond is tilted out of the anthracene plane by 1.6 and 3.6° . In 9,10-bis(phenylethynyl)anthracene,^{10b} the phenyl ring and the C=C bond are inclined to the anthracene plane by 25.7 and 3.7° , respectively. The long axes of all molecules in the triclinic structure of **5** are parallel within 0.3° , and their anthracene planes are parallel within 3.6° . The anthracene moieties are stacked in a brickwork pattern, with partial overlap between their outlying rings and a mean interplanar separation of *ca.* 3.4 Å.

Molecule **6** has no crystallographic symmetry and is substantially non-planar. The two benzene rings form a dihedral angle of 23.9° . The torsion angles between the benzene rings and their carboxy substituents are larger than in **2**, *viz.* 10.4° around the C(2)–C(3) bond and 13.2° around the C(16)–C(19) bond. It is noteworthy that the unsubstituted 1,4-diphenylbutadiyne is planar as a pure solid,²⁰ in co-crystals with perfluoro-1,4-diphenylbutadiyne,²¹ and in an acetylide Cu₄ cluster,²² whilst in 1,4-bis(4-nitrophenyl)butadiyne the two benzene rings are perpendicular.²³ However, the conformation has no appreciable effect on the bond distances in the butadiyne moiety, which coincide, within experimental error, in all diphenylbutadiyne derivatives, including **6**. All molecules in the triclinic structure of **6** have their long axes parallel. The packing motif can be described as strongly slanted stacks running parallel to the $[20\bar{1}]$ direction and comprising a brickwork-type layer. The mean interplanar separation in a stack is *ca.* 3.4 Å, and the shifts between adjacent molecules alternate between 5.6 and 7.8 Å in the directions almost parallel to the long molecular axes.

The closest intermolecular (C)H \cdots O contacts in structures **2** (2.67 – 2.70 Å), **5** (2.59 – 2.69 Å) and **6** (2.45 – 2.68 Å) are close to the sum of the van der Waals radii (2.68 Å)²⁴ and, according to MO calculations, are well within the range of stabilising C(sp²)–H \cdots O interactions (weak hydrogen bonds), which have a potential minimum at 2.58 Å.²⁵ However, structure **6** also contains an exceptionally short contact C(18)–H \cdots O(4') ($x+1, y, z$) of 2.22 Å, which nearly corresponds to the $E = 0$ point of the calculated potential curve²⁵ and the lower edge of the observed distribution of (C)H \cdots O distances,²⁴ *i.e.* to the border between stabilising and destabilising repulsive interactions.

Phase behaviour

The phase behaviour of compounds **2**–**6** was studied using differential thermal analysis (DTA) and transmitted polarised light microscopy (TPLM). The phase transition data are given in Table 2. Compounds **4** and **6** show two distinct crystalline phases upon heating. Only compound **4** was found to exhibit any stable liquid crystal mesophases: a nematic phase appeared

Table 2 Axial ratios and phase behaviour

Cpd	Axial ratio	Transitions upon heating	Transitions upon cooling
2	4.32	K 221.3 I	I 220.3 K ^a
3	5.90	K (233.5) ^b deg	—
4	5.26	K ₁ 216.7 K ₂ 233.6 N 320 deg	N 238.1 S/K ₂
5	2.68	K 291.1 I/deg	—
6	4.89	K ₁ 187.0 K ₂ (192.4) ^b I	I (188.9) ^b K

^a Metastable nematic phase forms on free cooling. ^b Observed by DTA only.

at 233.6 °C upon heating, which persisted until the sample degraded at 320 °C, a range of over 80 °C. Upon cooling, the nematic phase formed a transient smectic phase before crystallising. It is interesting that **4**, which has an axial ratio of 5.26 , exhibits mesophases whereas **3**, with a larger axial ratio of 5.90 , does not. This is likely due to the enhanced stability of the compound imparted by the four fluorine substituents on the central ring which allows the mesophase to form below the degradation temperature. Compound **2** exhibited a metastable nematic phase upon cooling.

Conclusion

A series of conjugated rigid rods containing carboxylate end groups have been prepared which are highly luminescent with quantum yields up to 0.9 . The 1,4-bis(4-carbomethoxyphenylethynyl)tetrafluorobenzene derivative displays a nematic mesophase over an 80 °C temperature range. Two of the derivatives were converted to their free carboxylic acids *via* the sodium salts. It is expected that these compounds will be of considerable utility in the construction of extended solids including transition metal carboxylates.

Experimental

All reactions were performed under a dry N₂ atmosphere using standard Schlenk techniques. Et₃N was freshly distilled from CaH₂ under N₂ prior to use. NMR spectra were recorded on Varian Mercury (¹H at 200 MHz, ¹³C{¹H} at 50 MHz, ¹⁹F{¹H} at 188 MHz) or Bruker Avance (¹H at 400 MHz, ¹³C{¹H} at 100 MHz) spectrometers, in CDCl₃, CD₂Cl₂, D₂O or d₆-DMSO. Chemical shifts for ¹³C and ¹H spectra are given in ppm relative to SiMe₄ as an external standard, using the solvent or residual protons therein for reference; ¹⁹F spectra are referenced to external CFC₃. FT-IR spectra were recorded as Nujol mulls on a Perkin-Elmer 1600 FT-IR spectrophotometer or a Bomen Michelson spectrophotometer. UV-Vis absorption spectra were recorded on an ATI Unicam UV-2 spectrophotometer. Steady state and time-resolved fluorescence measurements were performed at room temperature in dilute solutions, with an absorbance of <0.1 , using a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorimeter. Fluorescence quantum yields were determined at room temperature, relative to double matched standards [quinine sulfate in 0.1 M H₂SO₄ and 2,2'-(1,4-phenylene)bis(5-phenyl-oxazole) in cyclohexane],²⁶ and refractive index correction was performed.²⁷ Fluorescence lifetimes were recorded operating in the phase-modulation mode. The phase shift and modulation

were recorded over the frequency range 1–300 MHz, and the data fitted using the Jobin-Yvon software package. Mass spectra were recorded on an HP 5971 Mass Selective Detector attached to an HP 5890 GC using a 5% Ph-methylsiloxane coated capillary column with UHP helium as the carrier gas. Elemental analyses were obtained from M-H-W Laboratories, Phoenix, Arizona and the University of Durham. All organic reagents were obtained from commercial sources and tested for purity by GC–MS prior to use.

Synthesis

4-Ethynyl(methylbenzoate) (1)¹¹. A degassed solution of trimethylsilylacetylene (8.98 g, 91.6 mmol) in Et₃N (20 mL) was transferred *via* cannula into a Schlenk flask containing 4-iodo(methylbenzoate) (20 g, 76.3 mmol), CuI (0.29 g, 1.52 mmol) and Pd(PPh₃)₂Cl₂ (1.07g, 1.52 mmol) in Et₃N (400 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed *in vacuo*, and the residue dissolved in hexane and purified by passage through a short column of silica gel (70–230 mesh). The crude product was recrystallised from hexane. Yield 17.2 g (97%).

The above product (15.5 g, 66.8 mmol) was mixed with anhydrous sodium carbonate in MeOH (120 mL). The reaction mixture was stirred at room temperature for 3 h under N₂. The solvent was removed under reduced pressure and the crude 4-ethynyl(methylbenzoate) was purified by dissolution in hexane and passage through a short column of silica gel (70–230 mesh). Recrystallisation from hexane afforded pale yellow crystals.²⁸ Yield 8.70 g (81%), mp 93–94 °C (lit.¹¹ 92.5–93.5 °C). IR (cm⁻¹) 3239 (CH), 2103 (CC) 1703 (C=O), 1284 (COC). ¹H NMR (CDCl₃): δ 3.26 (1H, s, CCH), 3.91 (3H, s, CO₂CH₃), 7.51–7.59 (2H, m, ArH), 7.97–8.00 (2H, m, ArH). ¹³C{¹H} NMR (CDCl₃): δ 166.4 (CO), 132.1, 130.0, 129.6, 126.7, 82.8, 80.0, 52.2 (OCH₃). MS (EI), *m/z* (rel.): 160 (M⁺, 55), 129 (M⁺ – CH₃O, 100), 101 (54), 75 (27), 51 (10).

1,2-Bis(4-carbomethoxyphenyl)ethyne (2)¹³. Et₃N was transferred *via* syringe into a Schlenk flask containing 4-ethynyl(methylbenzoate) (2.30 g, 14.4 mmol), 4-iodo(methylbenzoate) (3.14 g, 12.0 mmol), CuI (0.046 g, 0.24 mmol) and Pd(PPh₃)₂Cl₂ (0.17 g, 0.24 mmol). The reaction mixture was stirred at room temperature for 2 h after which the solvent was removed *in vacuo*. The residue was dissolved in hot toluene and passed through a short pad of silica gel (70–230 mesh). The compound was obtained as colourless crystals on removal of toluene. Yield: 3.2 g (91%), mp 218–220 °C (lit.¹³ 219–223 °C). IR (cm⁻¹) 1718 (CO). ¹H NMR (CD₂Cl₂): δ 3.90 (6H, s, CO₂CH₃), 7.63 (4H, m, ArH), 8.02 (4H, m, ArH). ¹³C{¹H} NMR (CD₂Cl₂): δ 52.5 (OCH₃), 91.5 (CC), 127, 129, 130, 133, (ArC), 166 (CO). MS (EI), *m/z* (rel.): 295 (16), 294 (82), 264 (19), 263 (100), 176 (29). Anal. calc. for C₁₈H₁₄O₄: C, 73.46; H, 4.79. Found: C, 73.56; H, 4.80%.

1,4-Bis(4-carbomethoxyphenylethynyl)benzene (3). To a Schlenk flask containing 4-ethynyl(methylbenzoate) (0.768 g, 4.80 mmol), 1,4-diiodobenzene (0.660 g, 2.00 mmol), CuI (0.008 g, 0.042 mmol) and Pd(PPh₃)₂Cl₂ (0.028 g, 0.040 mmol)

under N₂ was added Et₃N (50 mL) *via* syringe. The reaction mixture was stirred overnight at room temperature. The resulting precipitate was collected by filtration, washed with water and dissolved in hot toluene. The hot toluene solution was filtered through a short pad of silica gel (70–230 mesh). Cooling of the toluene solution gave the desired compound as small, white crystals. Yield 0.36 g (46%), mp 234 °C (decomp.). IR (cm⁻¹) 1718 (CO). ¹H NMR (CDCl₃): δ 3.92 (s, 6H), 7.55 (d, 4H), 8.00 (m, 4H), 7.47 (s, 4H). MS (EI), *m/z* (rel.): 395 (32), 394 (100), 363 (33), 276 (17), 166 (17). Anal. calc. for C₂₆H₁₈O₄: C, 79.17; H, 4.60. Found: C, 79.38; H, 4.62%.

1,4-Bis(4-carbomethoxyphenylethynyl)-2,3,5,6-tetrafluorobenzene (4). Et₃N (40 mL) was added *via* a cannula to a degassed mixture of 4-ethynyl(methylbenzoate) (0.384 g, 2.4 mmol), 1,4-diiodotetrafluorobenzene (0.402 g, 1.0 mmol), Pd(PPh₃)₂Cl₂ (0.0337 g, 0.048 mmol), CuI (0.0091, 0.048 mmol) in a Schlenk flask. The reaction mixture was heated to reflux for 3 h. The resulting precipitate was collected by filtration, washed with water and dissolved in hot toluene, and the hot toluene solution was filtered through a short pad of silica gel (70–230 mesh). Cooling of the toluene solution gave the desired compound as small, white crystals. Yield 0.45 g (96%), mp 233–235 °C. IR (cm⁻¹) 1719 (CO). ¹H NMR (CDCl₃): δ 3.92 (s, 6H), 7.61 (m, 4H), 8.02 (m, 4H). ¹⁹F{¹H} NMR (CDCl₃): δ –147 (s). MS (EI), *m/z* (rel.): 467 (28), 466 (100), 436 (16), 435 (62), 348 (18), 202 (22). Anal. calc. for C₂₆H₁₄F₄O₄: C, 66.96; H, 3.03. Found: C, 66.91; H, 2.97%.

9,10-Bis(4-carbomethoxyphenylethynyl)anthracene (5). A Schlenk flask was charged with 9,10-diidoanthracene (0.430 g, 1.0 mmol), 4-ethynyl(methylbenzoate) (0.384 g, 2.4 mmol), Pd(PPh₃)₂Cl₂ (0.014 g, 0.02 mmol), CuI (0.004 g, 0.02 mmol) and evacuated and purged with N₂ three times. Dry triethylamine (40 mL) was added *via* cannula under N₂. The reaction mixture was stirred at room temperature for 3 h. The mixture was filtered, and the residue was dissolved in hot toluene and filtered through a 2 cm pad of neutral alumina. The filtrate was cooled to give orange/red crystals of the product. Yield: 0.40 g, (81%), mp 288–290 °C. IR (cm⁻¹) 1716 (CO). ¹H NMR (CDCl₃): δ 3.95 (s, 6H), 7.64 (m, 4H), 7.82 (m, 4H), 8.11 (m, 4H), 8.67 (m, 4H). MS (EI), *m/z* (rel.): 495 (39), 494 (100), 435 (8), 373 (9), 187 (15). Anal. calc. for C₃₄H₂₂O₄: C, 82.58; H, 4.48. Found: C, 82.43; H, 4.70%.

1,4-Bis(4-carbomethoxyphenyl)butadiyne (6). To a solution of 4-ethynyl(methylbenzoate) (1.08 g, 6.74 mmol) in ¹Pr₂NH (250 mL) under N₂ were added CuI (0.064 g, 0.34 mmol), Pd(PPh₃)₂Cl₂ (0.095 g, 0.135 mmol) and iodine (0.985 g, 3.88 mmol) while stirring. After vigorous stirring for 6 h, the solvent was removed *in vacuo*, and the residue was dissolved in hot toluene and purified by passage through a short column of silica gel (70–230 mesh). After removal of the toluene the residue was dissolved in CH₂Cl₂ (100 mL) and washed with saturated Na₂S₂O₃ (3 × 50 mL), and the organic layer was dried over MgSO₄. Removal of the solvent and recrystallisation from toluene gave the desired compound as a white powder. Yield 0.80 g (75%), mp 190–191 °C. IR (cm⁻¹) 1928 (CC). ¹H NMR (CDCl₃): δ 3.93 (s, 6H), 7.58 (m, 4H), 8.02 (m,

4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 52.3 (OCH_3), 76.2, 81.9 (CC), 126.1, 129.6, 130.6, 132.5 (ArC), 166.2 (CO). MS (EI), m/z (rel.): 318 (100), 287 (72), 200 (18), 128 (14). Anal. calc. for $\text{C}_{20}\text{H}_{14}\text{O}_4$: C, 75.46; H, 4.43. Found: C, 75.46; H, 4.48%.

1,2-Bis(4-benzoic acid)ethyne (7)²⁹. Compound **2** (0.95 g, 3.23 mmol) was dissolved in 40 mL of a 10% solution of NaOH in methanol. The reaction mixture was heated to reflux for 24 h, and allowed to cool. The sodium salt was filtered off as a white precipitate and dried *in vacuo*. Yield: 0.88 g (88%). ^1H NMR (D_2O): δ 7.48 (d, 4H), 7.70 (d, 4H).

The sodium salt was dissolved in water, and the solution acidified with HCl. The turbid solution was cooled and filtered and the solid was dried *in vacuo* to give 1,2-bis(4-benzoic acid)ethyne as a white powder. Yield: 0.48 g (64%). ^1H NMR (d_6 -DMSO): δ 7.69 (d, 4H), 7.97 (d, 4H).

1,4-Bis(4-carboxyphenylethynyl)benzene (8). Compound **3** (0.50 g, 1.27 mmol) was dissolved in 60 mL of a 20% solution of NaOH in methanol. The reaction mixture was heated to reflux for 24 h, and allowed to cool. The sodium salt was filtered off as a white precipitate and washed with methanol and the solid was dried *in vacuo*. Yield: 0.38 g (73%).

The sodium salt was dissolved in distilled water and acidified with HCl. The turbid solution was cooled in ice and filtered and dried *in vacuo* to give the diacid. Yield: 0.26 g (77%). ^1H NMR (DMSO): δ 7.67 (overlapped s and d, 8H), 7.96 (d, 4H).

X-Ray crystallography

Compound **2** was crystallised by slow evaporation of a hexane solution, compound **5** from hot CHCl_3 , and compound **6** by slow evaporation of a benzene solution. X-Ray diffraction data were collected on Bruker 3-circle diffractometers with SMART 1K CCD area detectors (for **2** and **5**) or a ProteumM APEX CCD area detector (for **6**), using graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) from a sealed tube (for **2** and **5**) or a 60W microfocussing Bede Microsource[®] with glass polycapillary optics (for **6**). The low temperature of the crystals was maintained using Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL³⁰ software. All C and O atoms were refined in anisotropic approximation, with H atoms 'riding' in idealized positions (**2** and **5**) or refined in isotropic approximation (**6**). Crystal data and experimental details are listed in Table 3.

CCDC reference numbers 249324–249326. See <http://www.rsc.org/suppdata/jm/b4/b413514h/> 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 liquid crystal transitions in samples having an approximate mass of 5 mg. The calorimeter was calibrated with an indium standard. Experiments were conducted in an environment of dry nitrogen, delivered through a cold finger at a flow rate of *ca.* 30 mL min^{-1} .

Table 3 Crystal data and experimental parameters for X-ray diffraction studies

Compound	2	5	6
Formula	$\text{C}_{18}\text{H}_{14}\text{O}_4$	$\text{C}_{34}\text{H}_{22}\text{O}_4$	$\text{C}_{20}\text{H}_{14}\text{O}_4$
Formula weight	294.29	494.52	318.31
T/K	160	110	120
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	$Pbca$	$P\bar{1}$	$P\bar{1}$
$a/\text{\AA}$	7.1061(8)	7.225(1)	7.0249(5)
$b/\text{\AA}$	5.9558(7)	11.660(1)	10.4613(8)
$c/\text{\AA}$	34.129(4)	15.381(1)	11.7016(8)
$\alpha/^\circ$	90	77.343(1)	75.204(3)
$\beta/^\circ$	90	83.037(1)	72.585(3)
$\gamma/^\circ$	90	72.026(1)	75.457(3)
$V/\text{\AA}^3$	1444.4(3)	1200.5(1)	779.0(1)
Z	4	2	2
$D_c/\text{g cm}^{-3}$	1.353	1.368	1.357
μ/mm^{-1}	0.096	0.089	0.095
$2\theta_{\text{max}}/^\circ$	56.5	55	61
Total reflections	8196	12 771	6778
Unique reflections	1667	5483	4305
Parameters	102	349	273
R_{int}	0.026	0.021	0.022
Reflections $I > 2\sigma(I)$	1365	4026	3456
$R [F, I > 2\sigma(I)]$	0.041	0.040	0.055
$wR (F^2, \text{all data})$	0.112	0.120	0.141

Thermographs were displayed on a PC and analysed using Mettler FP99 system software (version 1). All heating and cooling operations were carried out at $10 \text{ }^\circ\text{C min}^{-1}$ 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 $50 \text{ }^\circ\text{C}$; both were heated, at $10 \text{ }^\circ\text{C min}^{-1}$ to at least $5 \text{ }^\circ\text{C}$ above the sample's clearing/degradation temperature and cooled to $50 \text{ }^\circ\text{C}$ 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 identify 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.

To identify phase transitions, samples in powder form were held between BDH borosilicate coverslips (22 \times 22 mm; thickness No. 1). The glass was first cleaned by immersing in concentrated nitric acid for 1 h, followed by thorough rinsing in de-ionised water and then acetone. Following this, the clean coverslips were air-dried under a dust cover. Heating and cooling rates of $10 \text{ }^\circ\text{C min}^{-1}$ were typical and a dry N_2 purge was provided through the sample chamber at *ca.* 30 mL min^{-1} in an attempt to limit sample oxidation.

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Tolulope M. Fasina,^{*ab} Jonathan C. Collings,^a Jacqueline M. Burke,^a Andrei S. Batsanov,^a Richard M. Ward,^a David Albesa-Jové,^a Laurent Porrès,^a Andrew Beeby,^a Judith A. K. Howard,^a Andrew J. Scott,^c William Clegg,^c Stephen W. Watt,^{†d} Christopher Viney,^{‡d} and Todd B. Marder^{*a}

^aDepartment of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE. E-mail: Todd.Marder@durham.ac.uk; Fax: +44(191)-384-4737; Tel: +44(191)-334-2037

^bDepartment of Chemistry, University of Lagos, Lagos, Nigeria

^cSchool of Natural Sciences (Chemistry), University of Newcastle upon Tyne, Newcastle upon Tyne, UK NE1 7RU

^dDepartment of Chemistry, School of Engineering and Physical Sciences, Heriot-Watt University, Riccarton, Edinburgh, UK EH14 4AS

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