Gearing of Molecular Swirls: Columnar Packing of Nematogenic Hexakis(4alkoxyphenylethynyl)benzene Derivatives

Shern-Long Lee,^[b] Hsing-An Lin,^[a] Yi-Hui Lin,^[a] Hsiu-Hui Chen,^[a] Ching-Ting Liao,^[a] Tzu-Ling Lin,^[a] Yi-Chen Chu,^[b] Hsiu-Fu Hsu,^{*[a]} Chun-hsien Chen,^{*[b]} Jey-Jau Lee,^[c] Wen-Yi Hung,^[d] Qu-Yuan Liu,^[d] and Chunhung Wu^[a]



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Chem. Eur. J. 2011, 17, 792-799

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Abstract: Through molecular design and straightforward synthesis, incorporating an additional alkoxy chain onto various numbers of peripheral phenyls in nematogenic hexakis(4-alkoxyphenylethynyl)benzene was achieved to generate columnar phases with significantly expanded temperature ranges. For the compound with two decyloxy chains on every peripheral phenyl, scanning tunnelling microscopic studies indicate the molecule adopts a pre-

Keywords: columnar suprastructures • helical structures • liquid crystals • molecular swirls • scanning tunnelling microscopy ferred molecular-swirl geometry by restricting the conformational arrangement of the alkoxy side chains. Cooperative packing of the molecular swirls by a lock-in mechanism among columns results in a stable helical column packing evidenced by powder X-ray diffraction.

Introduction

Columnar liquid crystalline materials continuously attract interest because of their cooperative physical properties that lead to many technological applications.^[1] As for the design principles of columnar mesogenic materials, the molecular core planarity and chain density are usually the two main considerations, which result in columnar suprastructures that are generated mainly by planar disc-like mesogens with strong π - π core attractions and assisted by intermolecular forces, such as hydrogen bonding and dipole–dipole interactions.^[2] For example, a columnar packing was developed by replacing with biphenyls the peripheral phenyls in hexa(phenylethynyl)benzene 1,^[3] one of the most studied discotic nematogens, which would otherwise adopt a nematic mesophase due to reduced π - π interactions by the rotational freedom of the peripheral phenyls.

Recently, Meijer et al. reported oligo(*p*-phenylene vinylene) substituted star-like hexaarylbenzene compounds showing columnar packing in liquid crystalline states.^[4,5] Scanning tunnelling microscopic (STM) studies revealed molecular rosettes of specific chain "rotation directions" at a solid–liquid interface. Interdigitation of these chains from adjacent rosettes were attributed to the stability of 2D crystal structure, but was not utilised as the interaction for mesophase formation. On the other hand, we recently demonstrated that the

- [a] H.-A. Lin, Y.-H. Lin, Dr. H.-H. Chen, C.-T. Liao, T.-L. Lin, Prof. H.-F. Hsu, C. Wu
 Department of Chemistry Tamkang University, 251 Taipei (Taiwan)
 Fax: (+886) 02-2620-9924
 E-mail: hhsu@mail.tku.edu.tw
- [b] Dr. S.-L. Lee, Y.-C. Chu, Prof. C.-h. Chen Department of Chemistry National Taiwan University, 106 Taipei (Taiwan) Fax: (+886) 02-2363-6359 E-mail: chhchen@ntu.edu.tw
- [c] Dr. J.-J. Lee National Synchrotron Radiation Research Center of Taiwan 300 Hsinchu (Taiwan)
- [d] Prof. W.-Y. Hung, Q.-Y. Liu Institute of Optoelectronic Sciences National Taiwan Ocean University, 202 Keelung (Taiwan)
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002975.

side-arm rotation could be restricted and thus the interdisc interactions were improved by introducing an additional chain *ortho* to the original chain of one side-arm in **1**, and a discotic nematic (N_D) phase rather than the columnar packing was observed for **2**.^[6]

Reported herein is a very efficient reaction scheme that expedites further exploration of the restricted rotation to all six side-arms of the well-know nematogenic 1, in conjunction with application of interdigitation of chains with specific "rotation directions" for the generation of columnar suprasturctures. The resulting novel mesogens 5 should exhibit low melting points and wide mesogenic temperature ranges due to lateral substitution within the side arms. The rotation of peripheral phenyls, restricted but not rigid, endows structural flexibility for 5 to favour a cooperative fashion of chain arrangement giving a molecular swirl geometry, that is, a molecular rosette (Figure 1), to minimise intramolecular steric congestion. Hence, the interdisc π - π attractions are enhanced. Moreover, along the disc plane, packing of molecules of the same swirl sense, that is, a gearing or lock-in mechanism of molecular swirls, will be favoured to minimise steric crowdedness and in-plane interchain van der Waals (VDW) interactions can be maximised.

Results and Discussion

To investigate the influence of the dialkoxyphenylethynyl side arms on the mesophase properties in hexaynylbenznes, a varied number of dialkoxy-containing side arms were incorporated as shown in Scheme 1. Stoichiometric control of 1-ethynyl-4-hexyloxybenzene and higher reactivity of iodo group in 1,3,5-tribromo-2,4,6-triiodobenzene towards Sonogashira coupling enabled the successful synthesis of **3** (50%) and **4** (32%). Subsequent coupling of dialkoxy-containing side arms to **4** and **3** afforded compounds **5** and **6**, respectively. The synthesis of **7** originally suffered from low yields ($\approx 10\%$) when diisopropylamine was used as the base and the solvent. Various conditions were examined for the synthesis of **7** to give optimised yields ($\approx 50\%$) by using triethylamine as the base and triphenylphosphine as the auxillary ligand as detailed in experimental.

The mesogenic properties of 5, 6, and 7b, investigated by differential scanning calorimeter and optical polarizing mi-

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Figure 1. Top, molecular structures of 1, 1a, 2, and 7; bottom, schematic molecular geometry representations of compounds 1 and 7, in which cooperative and non-cooperative fashions of chain rotation in 7 are presented, showing sterically favoured and sterically congested conformations, respectively.

croscope, are listed in Table 1 together with those of $1a^{[6]}$ and $2^{[6]}$. As reported previously, replacing one side arm in 1a with a dialkoxy-containing side arm provided a N_D phase with lower transition temperatures and a wider mesophase range.^[6] In contrast, compounds 5, 6, and 7b, with two or more dialkoxy-containing side arms, exhibit a columnar phase while keeping the characteristics of a much lower melting point and wider mesophase range of 2. Hence, two dialkoxy-containing side arms are sufficient for the genera-

Table 1. Phase behaviors of compounds 1a and $2a \sim 2f$.^[a]

	Phase transition behaviour	$T [^{\circ}C] (\Delta H [kJ mol^{-1}])$	Range	
1 a ^[b]	Cryst-N _D -Iso _{p,d}	144 (37.7), 216 (0.1)	72	
2 ^[b]	Cryst-N _D -Iso _{p,d}	93.7 (65.72), 195.0	101	
5	Cryst-Col _r -Iso _{p.d.}	73.5 (47.57), 178	104	
6	Cryst-Col _r -Iso _{p.d.}	72.9 (40.31), 236	163	
7a (C ₄)	Cryst-Col _r -Iso _{p.d.}	137 (66.3), 232 (11.2)	95	
7b (C ₆)	Cryst–Col _r –Iso _{p.d.}	92 (115.3), 234 (11.1)	142	
7c (C ₈)	Cryst–Col _r –Iso _{p.d.}	79 (88.3), 227 (14.8)	148	
7d (C ₁₀)	Cryst-Col _r -Iso _{p.d.}	67 (118.9), 212 (13.8)	145	
7e (C ₁₂)	Cryst–Col _r –Iso	70 (195.7), 201 (14.4)	131	
$7f(C_{16})$	Cryst-Col _r -Iso _{nd}	74 (296.0), 169 (21.9)	95	

[a] Cryst, N_D, Col_r, Iso, and Iso_{p.d.} denote crystalline, discotic nematic, rectangular columnar, isotropic phases, and isotropic liquid with partial decomposition, respectively. All thermal data were obtained by DSC at a rate 10 °C min⁻¹. For **5**, **6** and **7a–d**, data were obtained from first heating runs and for **7e** and **7f** data were obtained from second heating runs. [b] See reference [5].

tion of columnar suprastructures. Compound **6** with three dialkoxy-containing side arms possesses the widest liquid crystalline range of 163°. The much lower melting points of **2**, **5**, **6**, and **7b** are attributed to their lower molecular symmetry and the lateral position of the added chains.^[6,7] Comparing with the monochain analogue (**1a**, 143.5–215.9 °C N_D), **7b** with a columnar phase exhibits a melting point 51° lower and a clearing point 18° higher to give a mesophase range of 69° wider. The generation of columnar suprastructures of **7b** is ascribed to the various aforementioned interactions, including the possible intercolumnar, swirl-gearing interactions.

In order to realise the possible swirl conformation as well as swirl-gearing interactions of 7, compound 7a with butyloxy chains was prepared in hope to obtain its X-ray single-crystal structure. However, attempts on growing single crystals of 7a gave very thin needles that were not suitable for X-ray structural determination.

The thermal properties of 7a-f are also given in Table 1. Most of these compounds showed partial decomposition prior to clearing, except the longer chain analogues 7e and 7f, which were enantiotropic; this enabled columnar phase determination from natural mesophase textures, birefringent dendritic or focal conic (Figure 2). The melting point de-



Figure 2. Optical micrographs of a) 6 at 183 °C and b) 7e at 170 °C sandwiched between glass slides showing dendritic or focal conic textures between cross polarisers.

creases with increasing chain length and remains at about 70 °C for derivatives with decyloxy chains or longer. The clearing temperature also decreases with increasing chain length, but not as significantly as the melting point. The two effects in the transition temperatures result in compounds with medium chain lengths, that is, hexyloxy, octyloxy, and decyloxy, possessing wider mesophase ranges than the shorter and longer chain analogues.



Scheme 1. Synthesis of compounds 5, 6 and 7a-f.

Single-crystal X-ray structural determination on 7a for the realisation of possible swirl molecular geometry was not achieved. Alternatively, to elucidate the development of molecular swirls for 7, STM (scanning tunneling microscopy) was employed to unveil possible orientations of the chains with respect to the core. The results show that these compounds adopted a face-on orientation and hexagonal arrangement on the basal plane of HOPG (highly orientated pyrolytic graphite). For those with decyloxy groups or shorter, for example, 7d, the chains were not resolved due to short alkyls being conformationally unsettled by their relatively weak van der Waals interactions with the substrate.^[8] A representation of the arrangement of alkoxy chains in 7e is shown in Figure 3; the liquid crystalline performance is in fact far superior to those with shorter chains. The dotted line in Figure 3a marks a domain boundary. Details of regimes I and II are shown in Figure 3b and c, respectively. The molecular cores were well resolved to give bright features of a pseudo-hexagon showing six peripheral phenyls around the central benzene as contrast to the dark characteristics exhibited by the chains. These brightness contrasts, **FULL PAPER**

corresponding to the degree of tunneling probability, were ascribed to the π -conjugated versus the saturated cores chains.^[8-10] Though not every chain was resolved, possibly due to some alkyls being floating as reported in the literature,^[10,11] most of them were recognised to establish the swirl molecular geometry by the bending directions of chains relative to the side-arm axes. As indicated by the arrows in Figure 3b and c, the senses of the molecular swirls are clearly revealed to be counter-clockwise and clockwise, respectively. The revolving of the peripheral phenyl planes on each side-arm axis is not resolved and hence the molecules were considered as 2D swirl discs rather than 3D helical structures. In contrast to the enantiomericity for 3D helices of opposite helical senses, a 2D molecular swirl will superimpose with its mirror image. However, when considering the graphite surface underneath, the 2D swirls of opposite rotation senses are chiral and enantiomeric to each other, even if the peripheral phenyl rings are coplanar with the central benzene.

The STM observations were limited in a quasi-two-dimensional system. The two reverse senses of swirls aggregated into their own respective domains in which the rotational senses of the swirls were the same within each domain to



Figure 3. STM images of **7e** on HOPG. a) A 40×28 nm image exhibiting a domain boundary indicated by the dotted line; 12×12 nm images in b) region I and c) region II, respectively, revealing counter-clockwise and clockwise rotational senses of alkoxy chains (arrows). The interdisc distance is measured to be 30 ± 2 Å after the calibration of the piezoelectric scanner.

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avoid steric congestions. At the junction of these two domains, a domain boundary with images of blurred disc and overlapped discs developed. The HOPG surface is known to influence strongly the organisation of monolayer above. Therefore, the 2D ordering of 7e influenced by the graphite surface underneath can be expected. However, reverse sense swirls aggregating into respective domains, resulting in domain separation, cannot be fully justified by HOPG surface induction. These observations support the proposition of the in-plane intermolecular correlations favouring the same swirl sense due to steric considerations.

The columnar mesophases of 5, 6, and 7a–f were probed by X-ray diffraction (XRD) studies and the results are tabulated in Table 2. All compounds show a broad halo at about 4.5 Å of molten chains indicating mesophase formation. Most compounds show signals indexed to d_{11} , d_{20} , d_{02} , and d_{31} , indicative of a rectangular arrangement of columns. For compounds 5, 7d, and 7e, only the halos d_{11} , and d_{20} were observed. However, a rectangular columnar phase was assigned due to their similar small-angle-signal patterns with respect to those of 7a and 7b and their similar optical tex-

Table 2. Powder X-ray diffraction data of compounds 7a-f.

	Т	Phase d space		ing [Å]	Miller	Lattice	$d_{\rm ntercol}$
	[°C]		obsd	calcd	indices	constants [Å]	[Å]
5	120	Col _{rd}	22.4	22.4	11	a = 36.48	23.8
			18.2	18.2	20	b = 28.30	
			4.5		alkyl		
6	100	Col _{rd}	22.7	22.7	11	a = 39.38	24.3
			19.7	19.7	20	b = 27.85	
			14.0	13.9	02		
			11.8	11.9	31		
			11.4	11.4	40		
			4.5		alkyl		
7a (C4)	180	Col _{rd}	20.9	20.9	11	a = 34.9	21.8
			17.4	17.4	20	b = 26.1	
			12.9	13.0	02		
			10.6	10.6	31		
			10.4	10.5	22		
			4.3	-	alkyl		
7b (C6)	180	Col _{rd}	23.2	23.2	11	a = 39.4	24.4
			19.7	19.7	20	b = 28.6	
			14.4	14.3	02		
			11.9	11.9	31		
			9.8	9.9	40		
			4.4	-	alkyl		
7c (C8)	190	Col _{rd}	25.4	25.4	11	a = 43.7	26.8
			21.9	21.9	20	b = 31.1	
			15.5	15.6	02		
			4.3	-	alkyl		
7d (C10)	133	Col _{rd}	28.2	28.2	11	a = 50.0	30.3
			25.5	25.0	20	b = 34.1	
			4.7	-	alkyl		
7e (C12)	180	Col _{rd}	28.4	28.4	11	a = 51.0	30.7
			25.5	25.5	20	b = 34.2	
			4.7	-	alkyl		
7 f (C16)	150	Col _{rd}	32.3	32.3	11	a = 60.0	36.6
			30.0	30.0	20	b = 38.3	
			17.7	17.7	31		
			15.0	15.0	40		
			4.6	-	alkyl		

tures. In the columnar phases of 5 and 6, the intercolumnar distances (d_{intercol}) of about 24.1 Å, one half of the rectangle diagonal, are significantly longer than the interdisc distance of 21.3 Å for the nematic phase of 1. For 1, the interdisc distance is slightly longer the rigid core size, indicating the chains were overlapping with adjacent molecular core. For 5 and 6, adjacent molecules were spaced out from each other to avoid interdisc chain/core overlap for the generation of columnar suprastructures. With the same chain length, compounds 5, 6, and 7b exhibit similar intercolumnar distances, indicating d_{intercol} is primarily dependent on the dialkoxycontaining side arms. The values of d_{intercol} of 7 do not correspond to, and are significantly shorter than, the calculated in-plane interdisc distances with full interdigitation of chains. As an example, when the chains are fully extended along the axis of the attached side arm for 7e, fully interdigitated all-trans chains between two adjacent columns will give a d_{intercol} of approximately 35.7 Å and the value from

XRD is 30.7 Å. The significant discrepancy between experimental and calculated intercolumnar distances can be realised by detailed analysis of the XRD results versus possible molecular packing fashions in the columnar phase. From the full interdigitation model, shortening d_{intercol} by further shifting the chains toward adjacent discs will destroy columnar packing. Hence, the shorter experimental d_{intercol} can only come from a nonfully-extended chain configuration, in-plane bending of chain axis from the axis of attached side arm, or out-ofplane bending of chain axis from the core plane. Non-fullyextended chain configuration can be excluded by the approximately regular increment of each C₂ lengthening of chains. Both the in-plane and out-of-plane chain bendings can be expected due to the bent ether linkage. The out-ofplane chain bending model can be ruled out, since the calculated d_{intercol} values, obtained by summing up the trans-O-to-O distance (19.1 Å) and $\cos(\theta)$ of chain length at various angle θ s, do not correlate with the experimental values. For in-plane chain bending, there is no simple mathematic equation for the estimation of intercolumnar distances for 7 with different bending angles, since the hexagonal cores also turn with different bending angles. Simulation of molecular packing has been used for the estimation of intercolumnar distances with various bending angles, 30, 60, 77, and 90°, for **7e.** The d_{intercol} for the bending angle of 77° was simulated for the comparison with the respective STM value. As the in-plane bending angle increases, the intercolumnar distance decreases, from 35.7 Å for 30° to 26.5 Å for 90° as the two limiting cases (Figure 4). The estimated intercolumnar distance of 30.2 Å with an in-plane bending of 77° is similar to the values of 30.4 and 30.0 Å determined by XRD and STM investigations, respectively. Similar simulations were also performed for the shorter and longer chain analogues 7a and **7**f with an in-plane bending angle of 77°. For **7**f, the d_{intercol} found by XRD is longer than that of calculated value, which implies a bending angle smaller than 77°. For 7a, the d_{intercol} value determined by XRD is significantly shorter than that by packing simulation, which may arise from a sig-

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Figure 4. Simulated two-molecule packing patterns of 7e with chain bending angles of a) 30°, b) 60°, c) 77°, and d) 90°. For clarity, only one chain is shown for each molecule.

correlation length of 4.6 Å, a pair of diffuse reflections, corresponding to a long π - π stacking distance of peripheral phenyls at 3.9 Å with an averaged tilting angle of 52°,^[4] appears at both sides of the meridian as shown in Figure 5b. The fact that the meridian-centred alkyl halos are perpendicular to the equator-centred intercolumnar reflections proves the out-of-plane chain-bending model to be invalid as described previously. At middle angles, a very weak diffuse reflection at 7.2 Å was detected, which cannot be derivative signals of the rectangular lattice due to its very diffuse nature. Apparent alignment of this scattering could not be unambiguously determined due to its very low intensity; however, the azimuthal scan of this scattering revealed the reflection centred along meridian rather than along the

nificantly larger bending angle. It should be noted that deviation from the cooperative fashion of in-plane chain bending model, one, two, or three chains bending to the opposite direction with respect to bending directions of other chains, will not give the experimentally observed in-plane rectangular lattices and will lead to significant longer intercolumnar distances and result in the experimentally observed in-plane rectangular lattice.

X-ray diffraction investigations on aligned 7e prepared by filament extrusion^[12] were utilised for the realisation of its possible helical packing. For comparison, Figure 5a and b show the XRD investigations on the unaligned sample of 7e. Figure 5c shows the 2D XRD pattern of an extruded filament of 7e. For this aligned sample, in the small-angle regime, a pair of sharp and intense arcs along the equator, corresponding to intercolumnar correlations, is found. Each arc consists of two overlapped reflections of d_{11} and d_{20} . Since the filament was placed vertically, these small-angle equatorial reflections correspond to the inter-columnar order. In the wide angle regime, in addition to the broad alkyl halo with a



Figure 5. Structural investigations of 7e by a) the 2D PXRD pattern of unaligned sample at 180°C (inset: 2D PXRD of small angle scatterings), b) respective intensity/2 θ plot of a), c) the 2D PXRD pattern of a sample aligned by filament extrusion at 105°C (inset: 2D PXRD of small angle scatterings), d) the azimuthal integration of the scattering intensity corresponding to the π -stacking distance, and e) the schematic illustration of the intramolecular arrangement of 7e within a helical column (* indicates a reference point on each disc to better illustrate the helical conformation within a column).

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equator, indicative of a modulation of electronic density along columns (Figure 5d).^[12,13] The distance is about twice that of the π - π stacking distance, indicating that every third disc within a column is rotationally correlated. With a C_6 rotational axis along the disc normal of **7** with a cooperative in-plane chain bending, such a correlation can be realised by rotating each successive stacked disc by $360^\circ/6/2 = 15^\circ$ about the C_6 axis to give a helical stacking with every other disc to be rotationally eclipsed (Figure 5e). Thus, the helical pitch can determined to be $7.2 \times 6 = 43.2$ Å.

The charge transport properties of **7c** and **7e** were investigated by the time-of-flight (TOF) transient-photocurrent technique.^[1,14] The samples for the TOF measurements were prepared by dissolving appropriate weight ratios (up to 25 wt%) of the compounds in chloroform and then dip-coating the solutions onto an ITO substrate to form amorphous films. Figure 6a presents the representative TOF transient for holes of **7c**, revealing dispersive transport behaviours.



Figure 6. a) Hole transient photocurrent signals for **7c** (thickness: $2.9 \,\mu$ m) at $E = 2.4 \times 10^5 \,\text{V cm}^{-1}$. Inset: double-logarithmic plots for determination of the transit times. b) Hole mobilities plotted as a function of the square root of the electric field.

The carrier transit time $(t_{\rm T})$ needed for determining carrier mobilities can be evaluated from the intersection point of two asymptotes in the double-logarithmic representation of the TOF transient. Figure 6b displays the field dependence of the carrier mobility of 7c and the hole mobility ranged from 1.5×10^{-4} to 2×10^{-4} cm²V⁻¹s⁻¹ for fields varying from 2.8×10^5 to 4.6×10^5 V cm⁻¹. The field dependence of hole mobility follows the nearly universal Poole-Frenkel relationship^[15]: $\mu \propto \exp(\beta E^{1/2})$, in which β is the Poole–Frenkel factor and $E^{1/2}$ is the square root of the electric field, which assumes that charge transport within amorphous organic solids by means of a hopping mechanism associated with energetic disorder of localised hopping sites and intermolecular positional disorder. For 7e, the TOF transient displays highly dispersive hole transport behavior and hence the carrier transit time could not be determined. The increase in the length of alkyl chains elongates the carrier hopping distance between molecules, leading to carrier trapping. Considering the non-fused molecular core of 7, the obtained fair hole mobility may arise from the high intermolecular correlations in the columnar phase.

Conclusion

In summary, through a straightforward and efficient synthesis, compounds **7** adopt a preferred molecular swirl geometry by restricting the conformational arrangement of alkoxy side chains, rather than inventing novel aromatic core structures for the generation of columnar suprastructures. Cooperative packing of the molecular swirls by a lock-in mechanism among columns results in a stable columnar mesophase, the temperature range of which becomes twice that of the prototypical **1**. The molecular design may be applied to other discotic nematogens for pursuing columnar packing motifs in further optoelectronic applications in which ordered disc packing along and perpendicular to the molecular plane is required.

Experimental Section

All chemicals and solvents were reagent grades (Aldrich Chemical Co.) and used without further purification. ¹H and ¹³C NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts are reported in ppm relative to residual CHCl₃ (¹H: $\delta = 7.26$ ppm; ¹³C: $\delta = 77.0$ ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Absorption spectra were recorded with a Jasco V-550 spectrometer. Photoluminescence spectra were recorded with a Hitachi F-2500 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer Pyris1 with heating and cooling rates of 5 and 10 °C min⁻¹. Polarizing optical microscopy (POM) was carried out on a Zeiss Axio Imager A1m with a Mettler FP90/ FP82HT hot stage system. X-ray powder diffraction data were collected on the wiggler beam line BL17 A of the National Synchrotron Radiation Research Center (NSRRC; Taiwan), using a triangular bent Si(111) monochromator and a wavelength of 1.3271 Å. The sample in a 1 mm capillary or an extruded filament was mounted on the Huber 5020 diffractometer. The BL17 A beamline was equipped with an air-stream heater and the temperature controller was programmed by a PC with a PID feedback system. Scanning tunneling microscopy (STM) experiments were carried out with a PicoScan 4500 controller (Agilent Technologies) and using commercially available Pt/Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments). The substrate was HOPG (SPI, ZYH) and the images of bare HOPG were employed for the piezoelectric calibration of the x and y displacement per volt. The samples for STM imaging were prepared by placing on HOPG a 50 µL aliquot of 7 (1 mg) dissolved in phenyloctane (1 mL). Typical imaging conditions of bias voltage and tunneling current were 0.1-1.0 V and 0.01-0.20 nA, respectively. The images were subjected to minimal flattening to reduce noise (WSxM, Nanotech Electronica). For the TOF measurements, the samples were mounted in a cryostat under vacuum (ca. 10⁻³ Torr). A pulsed nitrogen tunable dye laser was used as the excitation light source (to match the absorption of organic films) through the semitransparent electrode (ITO) induced photogeneration of a thin sheet of excess carriers. Under an applied dc bias, the transient photocurrent was swept across the bulk of the organic film toward the collection electrode (Ag), and then recorded with a digital storage oscilloscope. Depending on the polarity of the applied bias, selected carriers (holes or electrons) are swept across the sample with a transit time of t_{T} . With the applied bias V and the sample thickness D, the applied electric field E is V/D, and the carrier mobility is then given by $\mu = D/(t_T E) = D^2/(V t_T)$, from which the carrier transit time $(t_{\rm T})$ can be extracted from the intersection point of two asymptotes to the plateau and the tail sections in double-logarithmic plots. Mass spectra were obtained on Finnegan MAT-95XL and elemental analyses were carried out on a Heraeus CHN-O-Rapid Analyzer at the NSC Regional Instrumental Center at National Chiao Tung University, Hsinchu (Taiwan) and at National Cheng Kung University, Tainan (Taiwan).

Hexakis(3,4-dialkoxyphenylethynyl)benzene (7): 1,2-Dialkoxy-4-ethynylbenzene (2.172 mmol) in triethylamine (8 mL) wasa added dropwise to a mixture of *trans*-dichlorobis(triphenylphosphine)palladium(II) (13 mg, 0.019 mmol), copper iodide (8 mg, 0.04 mmol), triphenylphosphine (10 mg, 0.038 mmol), hexabromobenzene (100 mg, 0.181 mmol), triethylamine (8 mL), and tetrahydrofuran (8 mL) under a nitrogen atmosphere under reflux. The mixture was stirred under reflux for 12 h. After cooling, dichloromethane (100 mL) was added. The mixture was washed with saturated NH₄Cl(aq) (40 mL), $4 \times \text{HCl}(aq)$ (40 mL×3) and H₂O (50 mL×3) and dried over MgSO₄. After removal of the solvents, the residue was purified by crystallisation from hot ethyl acetate. When necessary, the product was further purified by column chromatography (SiO₂, *n*-hexane/dichloromethane 5:1) and crystallised from *n*-hexane to yield **7** as a yellow powder (yield 8–59%).

Data for 7e: Yield: 21 %. ¹H NMR (CDCl₃, 300 MHz): δ =7.21 (dd, *J*= 8.4, 1.8 Hz, 6H), 7.12 (d, *J*=1.5 Hz, 6H), 6.81 (d, *J*=8.4 Hz, 6H), 4.01 (t, *J*=6.5 Hz, 12H), 3.83 (t, *J*=6.5 Hz, 12H), 1.84 (m, 12H), 1.74 (m, 12H), 1.47 (m, 24H), 1.34 (m, 192H), 0.89 ppm (m, 36H); ¹³C NMR (CDCl₃, 75 MHz): δ =150.1, 148.9, 126.9, 125.0, 116.7, 115.5, 113.1, 99.4, 86.3, 69.2, 69.1, 31.93, 29.77, 29.71, 29.65, 29.56, 29.48, 29.39, 29.36, 29.29, 26.13, 26.07, 22.68, 14.01 ppm; MS (FAB+): *m*/z calcd for C₁₉₈H₃₁₈O₁₂: C 890.64; found 2890.56; elemental analysis calcd (%) for C₁₉₈H₃₁₈O₁₂: C 82.27, H 11.09; found: C 82.27, H 11.08.

Acknowledgements

We thank the National Science Council of Taiwan (NSC 96-2628M-032 and NSC 99-2628M-002-013) for supporting this work.

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Received: October 15, 2010 Published online: January 5, 2011