Supporting Information

Facile Transformation of 1-Aryltriphenylenes into Dibenzo[fg,op]tetracenes by Intramolecular Scholl Cyclodehydrogenation: Synthesis, Self-Assembly, and Charge

Carrier Mobility of Large π -Extended Discogens

Ke-Qing Zhao,^{1,*}, Min Jing,¹ Ling-Ling An,¹ Jun-Qi Du,¹ Yan-Hong Wang,¹ Ping Hu,¹ Bi-Qin Wang,¹ Hirosato Monobe,^{2,*} Benoît Heinrich,³ Bertrand Donnio^{3,*}

[1] College of Chemistry and Material Science, Sichuan Normal University, Chengdu 610066, China.

E-mail: kqzhao@sicnu.edu.cn

[2] Inorganic Functional Materials Research Institute, National Institute of Advanced

Industrial Science and Technology (AIST), Ikeda, Osaka 5638577, Japan.

E-mail: monobe-hirosato@aist.go.jp

[3] Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), CNRS-Université de

Strasbourg (UMR 7504), 23 rue du Loess, BP 43, 67034 Strasbourg Cedex 2 (France)

E-mail: bertrand.donnio@ipcms.unistra.fr

Table of Content

1. Experimental Techniques	Pages 2-3
2. Polarizing Optical Texture	Pages 3-6
3. DSC	Pages 6-10
4. ¹ H NMR	Pages 11-25
5. Mass Spectra	Pages 26-38
6. IR	Page 39
7. SAXS	Pages 39-45
8. Frontier Orbital	Page 46
9. Concentration-dependent ¹ H NMR investigation	Pages 47-48
10. Structurally related dibenzo[fg,op]tetracene discogens	Page 49

1. Experimental Techniques

¹**H NMR** was measured on a Varian INOVA 400 MHz spectrometer or a Bruker-Advance-600 NMR spectrometer in CDCl₃ using TMS as the internal standard.

IR spectra were recorded on a Perkin Elmer 16 PC FTIR spectrometer.

The high-resolution mass spectra were measured on a Fourier Transform ion cyclotron resonance mass spectrometer (7.0T **FTICR-MS**) instrument made by IonSpec (Varian now) with MALDI or ESI as the ion source.

Elemental analyses were performed on a Carlo Erba 1106 elemental analysis apparatus.

UV/Vis absorption spectra were recorded on a Perkin Elmer UV/VIS/NIR Spectrometer Lambda 950.

Fluorescence was measured a HORIBA Fluoromax-4p (FM4PC), and the quantum efficiencies were measured by a HORIB-F-3029 Integrating Sphere, HORIBA, Kyoto, Japan, by the optical dilute method reported by Demas and Crosby.¹

The optical textures of liquid crystals were observed using a XP-201 and an Olympus BH_2 Polarised Optical Microscope (**POM**) equipped with a XP-201 and Mettler FP82HT hotstages of which temperatures were controlled by a XPR-201 and Mettler FP90.

The phase transition temperatures and enthalpies were investigated using a TA-DSC Q100 differential scanning calorimeter (**DSC**) under N_2 atmosphere with heating or cooling rate of 10°C/min.

Most temperature-variation **SAXS** experiments were performed on a Rigaku Smartlab (3) X-Ray diffractometer equipped with a TCU 110 temperature control unit. The sample temperature was controlled within ± 1 K. The X-ray sources (Cu K α , $\lambda = 0.154$ nm) were provided by 40 kW ceramic tubes. SAXS patterns of **31** and **4i** were recorded with a linear monochromatic Cu K α 1 beam ($\lambda = 1.5405$ Å) obtained using a sealed-tube generator (600 W) equipped with a bent quartz monochromator. Patterns were recorded with a curved Inel CPS 120 counter gas-filled detector linked to a data acquisition computer; periodicities up to 70 Å can be measured, and the sample temperature controlled to within ±0.01 °C from 20 to 200 °C.

¹ J. N. Demas, G. A. Crosby, J. Phys. Chem., 1971, 75, 991-1024.

The crude powder was filled in Lindemann capillaries of 1 mm diameter and 10 μ m wall thickness and exposure times were varied from 1 to 24 h.

Electron and hole mobilities were measured by a **TOF** (time-of-flight) technique using a N₂ gas laser (KEN-1520, Usho, 600 ps pulse width, $\lambda = 337$ nm) and a hot stage. The cell with indium-tin-oxide (ITO) electrodes was mounted on a handmade hot stage, and electric bias was applied by dry cell batteries. Depending on the polarity of the applied electric field (20 to 50 kV/cm), positive or negative charge carriers were moving through the sample, causing displacement photocurrent, which was detected on a digital oscilloscope (DSO5052A, Agilent Technology) with a commercially available current amplifier (DHPCA-100, FEMTO). A schematic diagram of the experimental setup is shown in Figures A and B. The cells (16.8 and 16.2 µm-thick) were filled with the material in its isotropic liquid state by capillary forces, and then cooled down to the lamella-columnar phase. POM showed a highly birefringent texture practically with no homeotropic domains. The laser focused on a spot with homeotropic aligned sample area.



2. Polarizing Optical Microscopic Textures







Figure 1S. POM images of 1-aryltriphenylenes (**3**) and corresponding cyclodibenzo[fg,op]tetracenes (**4**).

3. Differential Scanning Calorimetry (DSC)









Figure 2S. DSC curves of 1-aryltriphenylenes (3) and corresponding dibenzo[fg,op]tetracenes (4). The DSC were measured with heating and cooling rate of 10 °C min⁻¹ in a N_2 atmosphere.

	1st heating	1st cooling	2nd heating
3a	Cr ₁ 73 (4.1) Cr ₂ 81 (25.2) Col _{hex} 105 (4.4) I	I 103 (4.5) Col _{hex} 30 (11.5) Cr	Cr 83 (31.1) Col _{hex} 106 (5.0) I
3b	Cr 99 (30.5) Col _{hex} 112 (6.5) I	I 109 (5.0) Col _{hex} 38 (9.4) Cr	Cr 90 (21.1) Col _{hex} 111 (5.0) I
3c	Cr 113 (47.6) I	I 87 (6.6) Col _{hex} 65 (28.8) Cr	Cr 112 (48.0) I
3d	Cr 119 (50.4) I	I 111 (6.5) Col _{hex} 48 (10.6) Cr	Cr ₁ 111 (9.2) Cr ₂ 120 (42.9) I
3e	$Cr_1 109 (1.2) Cr_2 114 (17.2) Col_{hex} 119 (4.1) I$	I 116 (6.6) Col _{hex} 66 (16.4) Cr	Cr 113 (26.3) Col _{hex} 118 (6.3) I
3f	Cr ₁ 46 (2.6) Cr ₂ 70 (34.9) I	I 44 (3.4) Col _{hex} 6 (4.4) Cr	Cr 71 (42.9) I
3g	Cr ₁ -11 (6.2) Cr ₂ 57 (14.2) Col _{hex} 80 (4.4) I	I 77 (3.2) Col _{hex}	Cr 26 (4.5) Col _{hex} 80 (3.3) I
3h	Cr 92 (40.9) I	I 69 (25.7) Cr	Cr 91 (28.0) I
3i	Cr ₁ 57 (33.2) Cr ₂ 88 (28.7) Cr ₃ 96 (1.1) I	I 63 (23.4) Cr	Cr ₁ 88 (28.1) Cr ₂ 97 (1.72) I
3j	Cr 75 (35.3) I	I 49 (1.9) Col _{hex} 27 (18.3) Cr	Cr ₁ 53 (9.6) Cr ₂ 74 (22.2) I
3k	Cr 77 (36.4) I	I 69 (4.3) Col _{hex}	Cr ₁ 66 (10.9) Cr ₂ 71 (3.4) Cr ₃ 77 (2.6) I
31	Cr 115 (30.1) Col _{hex} 159 (5.5) I	I 156 (5.4) Col _{hex} 56 (18.9) Cr	Cr 110 (32.7) Col _{hex} 158 (5.6) I
3m	Cr ₁ 30 (0.9) Cr ₂ 98 (33.5) I	I 78 (5.5) Col _{hex} 49 (13.6) Cr	Cr 97 (31.6) I
3n	$Cr_1 50 (7.7) Cr_2 60 (16.3) Col_{hex} 79 (4.0) I$	I 76 (4.1) Col _{hex} 11 (15.6) Cr	Cr 71 (23.8) Col _{hex} 81 (4.0) I
4 a	Cr 48 (21.5) Col _{hex} 105 (5.3) I	I 103 (5.0) Col _{hex}	Col _{hex} 105 (5.1) I
4b	Cr 52 (29.1) Col _{hex} 142 (7.2) I	I 140 (5.5) Col _{hex}	Col _{hex} 142 (5.5) I
4c	Cr ₁ 51 (2.3) Cr ₂ 78 (26.7) I	_c	Cr 78 (21.0) I
4e	$Cr_1 57 (6.2) Cr_2 74 (11.8) Col_{hex} 152 (5.9) I$	I 149 (6.1) Col _{hex}	Col _{hex} 152 (6.2) I
4f	Cr 54 (18.9) Col _{hex} 66 (6.9) I	I 64 (5.6) Col _{hex}	Col _{hex} 66 (5.7) I
4g	Col _{hex} 67 (7.2) I	I 63 (4.5) Col _{hex}	Col _{hex} 66 (4.5) I
4h	Col _{hex} 106 (8.1) I	I 101 (5.4) Col _{hex}	Col _{hex} 104 (5.5) I
4i	Cr ₁ -27 (6.7) Cr ₂ 82 (37.4) I	I 64 (5.2) Col _{hex} 42 (18.3) Cr ₂ -36 (6.7) Cr ₁	Cr ₁ -28 (7.5) Cr ₂ 81 (35.0) I
4j	Col _{hex} 72 (7.3) I	I 69 (5.7) Col _{hex}	Col _{hex} 72 (5.6) I
4k	Col _{hex} 83 (8.1) I	I 79 (6.2) Col _{hex}	Col _{hex} 82 (6.2) I
4n	Col _{hex} 80 I ^b	I 78 Col _{hex} ^b	

Table 1S. Mesophases, phase transition temperatures, and enthalpy changes of compounds **3** and **4** measured by DSC (N₂, heating and cooling rate 10 °C min⁻¹) ^a

^a Cr, crystalline solid phase; Col_{hex}, columnar hexagonal mesophase; I, isotropic liquid. ^b Measured by polarizing optical microscopy with heating plate. 4. NMR







Figure 3S2. ¹H NMR spectrum of **3a**



















ppm (t1)

Figure 3S6. ¹³C NMR spectrum of **4b**



ppm (f1)











Figure 3S9. ¹H NMR spectrum of **3d**











Figure 3S12. ¹H NMR spectrum of **3f**











Figure 3S15. ¹H NMR spectrum of **4g**



Figure 3S16. ¹H NMR spectrum of **3h**



Figure 3S18. ¹³C NMR spectrum of **4h**





Figure 3S20. ¹H NMR spectrum of **4i**



ppm (f1)

Figure 3S21. ¹³C NMR spectrum of **4i**



Figure 3S22. ¹H NMR spectrum of **3**j



















ppm (t1)

Figure 3S27. ¹H NMR spectrum of **4**k







Figure 3S29. ¹H NMR spectrum of **4n**

5. Mass Spectra







Figure 4S2. HRMS spectrum of 4a



Ρ







Figure 4S4. HRMS spectrum of 4b



Figure 4S5. HRMS spectrum of 4c



Figure 4S6. HRMS spectrum of 4c







Figure 4S7. HRMS spectrum of 3d



Figure 4S8. HRMS spectrum of 3d







Figure 4S9. HRMS spectrum of 4e



Figure 4S10. HRMS spectrum of 4e



Figure 4S11. HRMS spectrum of 4f



Figure 4S12. HRMS spectrum of 4f



Figure 4S13. HRMS spectrum of 4g



Figure 4S14. HRMS spectrum of 4g



Figure 4S15. HRMS spectrum of 4h



Figure 4S16. HRMS spectrum of 4h



Figure 4S18. HRMS spectrum of 4j







Figure 4S19. HRMS spectrum of 4j



Figure 4S20. HRMS spectrum of 4k







Figure 4S21. HRMS spectrum of 4k



Figure 4S22. HRMS spectrum of 3I





Date: 04-MAY-2014 Time: 14:18:16 Scale: 9.6051







Figure 4S24. HRMS spectrum of 3m







Figure 4S25. HRMS spectrum of 3n



Figure 4S26. HRMS spectrum of **3n**





Figure 5S. IR spectra of 1, 3f and 3l

7. SAXS



Figure 6S1. SAXS patterns of **3b** at various temperatures



Figure 6S2. SAXS patterns of 3l at various temperatures



Figure 6S3. SAXS patterns of 4b at various temperatures



Figure 6S4. SAXS patterns of 4h at various temperatures



Figure 6S5. SAXS patterns of 4i at various temperatures



Figure 6S4. Representative SAXS patterns of some terms of series **3**: **3b** at 55°C, **3k** at 25°C, and **3l** at 120°C (h_{ar} , h_{ch} , h_{tp} are defined in text).





Figure 6S5. SAXS patterns of some representative terms of series 4 (all at 25°C; h_{ch} , h_{π} are defined in text).

Cpds	T (°C)	d _{meas.} (Å)	hk	d _{calc.} (Å)	Phase and
					parameters
3b	55	16.76	10	16.77	Col _{hex}
		9.68	11	9.68	a = 19.36 Å
		8.40	20	8.39	$S_{col} = 324.7 \text{ Å}^2$
		6.34	21	6.34	$V_{mol} = 1360 \text{ Å}^3$
		5.30-4.00	h_{ar} + h_{ch} + h_{tp}	-	$h_{mol} = 4.2 \text{ Å}$
3k	25	17.14	10	17.14	Col _{hex}
		9.89	11	9.00	a = 19.79 Å
		8.56	20	8.57	$S_{col} = 339.4 \text{ Å}^2$
		5.30-4.00	h_{ar} + h_{ch} + h_{tp}	-	$V_{mol} = 1336 \text{ Å}^3$
					$h_{mol} = 3.9 \text{ Å}$
31	120	16.92	10	16.90	Col _{hex}
		9.77	11	9.76	a = 19.54 Å
		8.43	20	8.45	$S_{col} = 331.0 \text{ Å}^2$
		4.80-4.00	h_{ar} + h_{ch} + h_{tp}	-	$V_{mol} = 1430 \text{ Å}^3$
					$h_{mol} = 4.3 \text{ Å}$
3f	25	17.01	10	17.01	Col _{hex}
		9.83	11	9.82	a = 19.64 Å
		8.50	20	8.50	$S_{col} = 334.1 \text{ Å}^2$
		5.30-4.00	h_{ar} + h_{ch} + h_{tp}	-	$V_{mol} = 1309 \text{ Å}^3$
					$h_{mol} = 3.9 \text{ Å}$
4b	25	17.48	10	17.47	Col _{hex}
		10.09	11	10.09	a = 20.18 Å
		8.73	20	8.74	$S_{col} = 352.5 \text{ Å}^2$
		6.61	21	6.60	$V_{mol} = 1319 \text{ Å}^3$
		4.50-4.40	h _{ch}	-	$h_{mol} = 3.74 \text{ Å}$

Table 2S. SAXS results of representative 1-aryltriphenylenes and dibenzo[fg,op]tetracenes

		3.65	h _π	-	
4e	25	17.30	10	17.33	Col _{hex}
		9.96	11	10.00	a = 20.01 Å
		8.66	20	8.66	$S_{col} = 346.8 \text{ Å}^2$
		6.59	21	6.55	$V_{mol} = 1339 \text{ Å}^3$
		4.40-4.30	h _{ch}	-	$h_{mol} = 3.86 \text{ Å}$
		3.61	h_{π}	-	
4f	25	17.52	10	17.52	Col _{hex}
		10.11	11	10.11	a = 20.23 Å
		8.76	20	8.76	$S_{col} = 354.4 \text{ Å}^2$
		6.62	21	6.62	$V_{mol} = 1298 \text{ Å}^3$
		4.40-4.30	h _{ch}	-	$h_{mol} = 3.66 \text{ Å}$
		3.63	h_{π}	-	
4j	25	17.31	10	17.38	Col _{hex}
		9.99	11	10.03	a = 20.06 Å
		8.70	20	8.69	$S_{col} = 348.8 \text{ Å}^2$
		6.62	21	6.57	$V_{mol} = 1331 \text{ Å}^3$
		4.40-4.30	h _{ch}	-	$h_{mol} = 3.82 \text{ Å}$
		3.59	h_{π}	-	
4k	25	17.34	10	17.36	Col _{hex}
		10.0	11	10.03	a = 20.04 Å
		8.67	20	8.68	$S_{col} = 348.0 \text{ Å}^2$
		6.60	21	6.56	$V_{mol} = 1325 \text{ Å}^3$
		4.40-4.30	h _{ch}	-	$h_{mol} = 3.81 \text{ Å}$
		3.59	h_{π}	-	
4h	25	18.91	10	19.00	Col _{hex}
		10.98	11	10.97	a = 21.94 Å
		9.53	20	9.50	$S_{col} = 416.8 \text{ Å}^2$
		7.18	21	7.18	$V_{mol} = 1585 \text{ Å}^3$
		4.40-4.30	h _{ch}	-	$h_{mol} = 3.80 \text{ Å}$
		3.61	h_{π}	-	

 $d_{meas.}$ and $d_{calc.}$ are the experimentally measured and calculated diffraction distances [Å]; *hk* are the Miller indices of the reflections; h_{ch} , h_{ar} , h_{tp} and h_{π} correspond to the maximum of the diffuse scattering due to lateral distances between molten aliphatic tails (h_{ch}), between the average stacking periodicity between rigid triphenylene core and aryl unit ($h_{tp} + h_{ar}$), and DBT units (h_{π}), respectively; $d_{calc.}$ calculated spacing from optimized lattice parameter; a is the lattice parameters of the hexagonal lattice; deduced from the following mathematical expressions: $a = 2x \sum [d_{hk}(h^2+k^2+hk)^{1/2}(N_{hk}\sqrt{3})^{-1}]$, where N_{hk} is the number of hk reflections for the Col_{hex} phase; V_{mol} is the molecular volume, S_{col} is the lattice area and $h_{mol} = V_{mol}/S_{col}$ is the molecular

8. Frontier Orbital

The molecular structures of **3i** and **4i** were calculated by Gaussian09 at the level of B3L YP/6-31G**, and their most stable configurations were obtained. Their frontier molecular orbital energies and the gaps yielded: **3i**: HOMO, -4.837eV, LUMO, -0.509eV; energy gap: 4.228eV; **4i**: HOMO, -4.840eV; LUMO, -0.940eV; energy gap: 3.800eV. Quantum chemistry calculation results show that, compared to **3i**, the fused dibenzo[fg,op]tetracene **4i** exists more symmetrical frontier molecular orbitals, therefore improved pi-pi stacking and higher charge carrier transport are expected.



Figure 7S. Frontier Molecular Orbitals: HOMO and LUMO A: **3i**, HOMO; B: **3i**, LUMO C: **4i**, HOMO; D: **4i**, LUMO

9. Concentration-dependent ¹H NMR investigation

The self-assembly behavior in solution of 1-aryltriphenylenes **3** (**3b** and **3i**) and the planar π -extended tetracenes **4** (**4b** and **4i**) were studied in various concentrations by ¹H NMR. The results show that both **3** and **4** do not display π - π staking aggregation in deuterated chloroform.





Figure 8S. Concentration-dependent ¹H NMR spectra of **3b**, **4b**, **3i** and **4i**.

10. Structurally related dibenzo[fg,op]tetracene discogens



Figure 9S. Chemical structures of reported dibenzo[fg,op]tetracene discogens. See references 27, 29, 30, respectively from the manuscript.