Supporting Information for:

Thienoacene dimers based on the thieno[3,2-*b*]thiophene moiety: Synthesis, Characterization and Electronic Properties

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Figure. S1. ^{1}H NMR spectra of **7** in $CDCl_3$ (25°C)

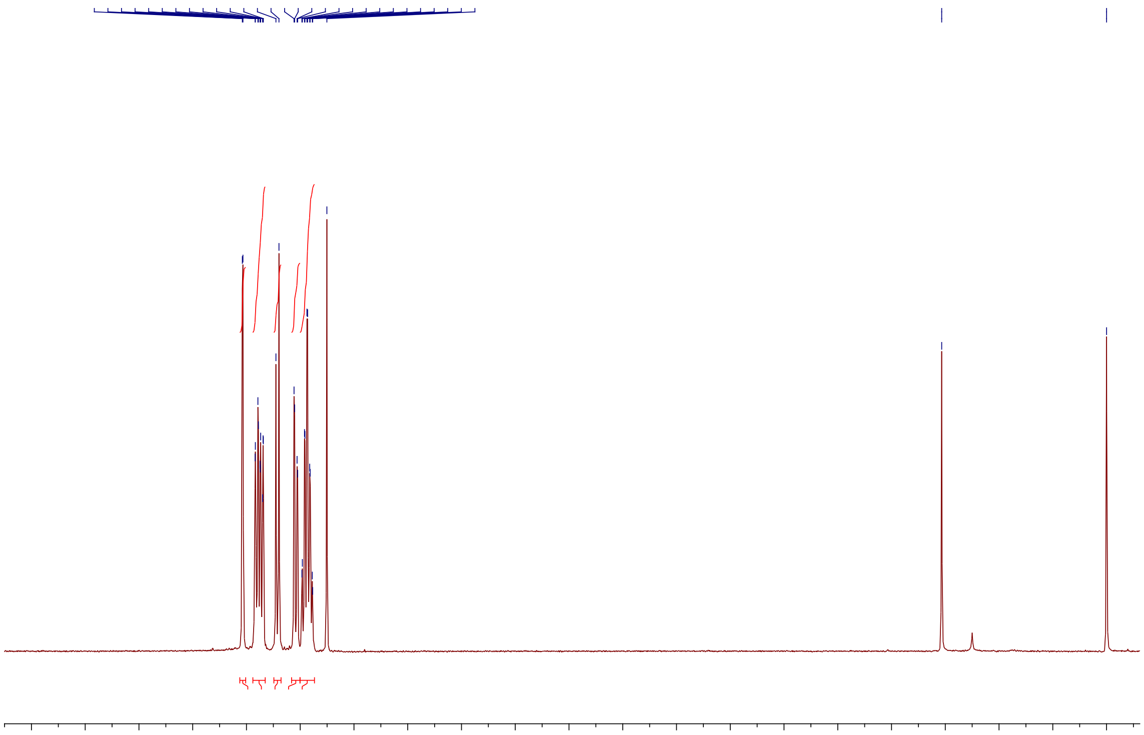


Figure. S2. ^{13}C NMR spectra of **7** in $CDCl_3$ (25°C)

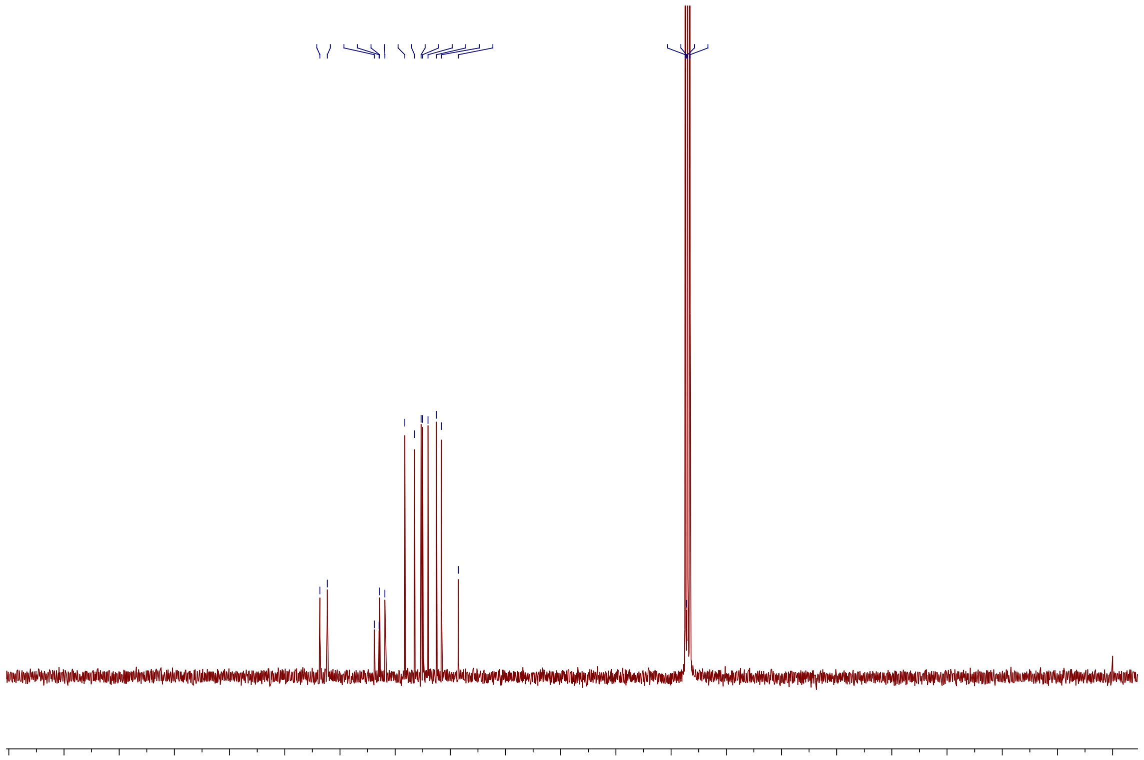


Figure. S3. ^{1}H NMR spectra of **8** in $CDCl_3$ (25°C)

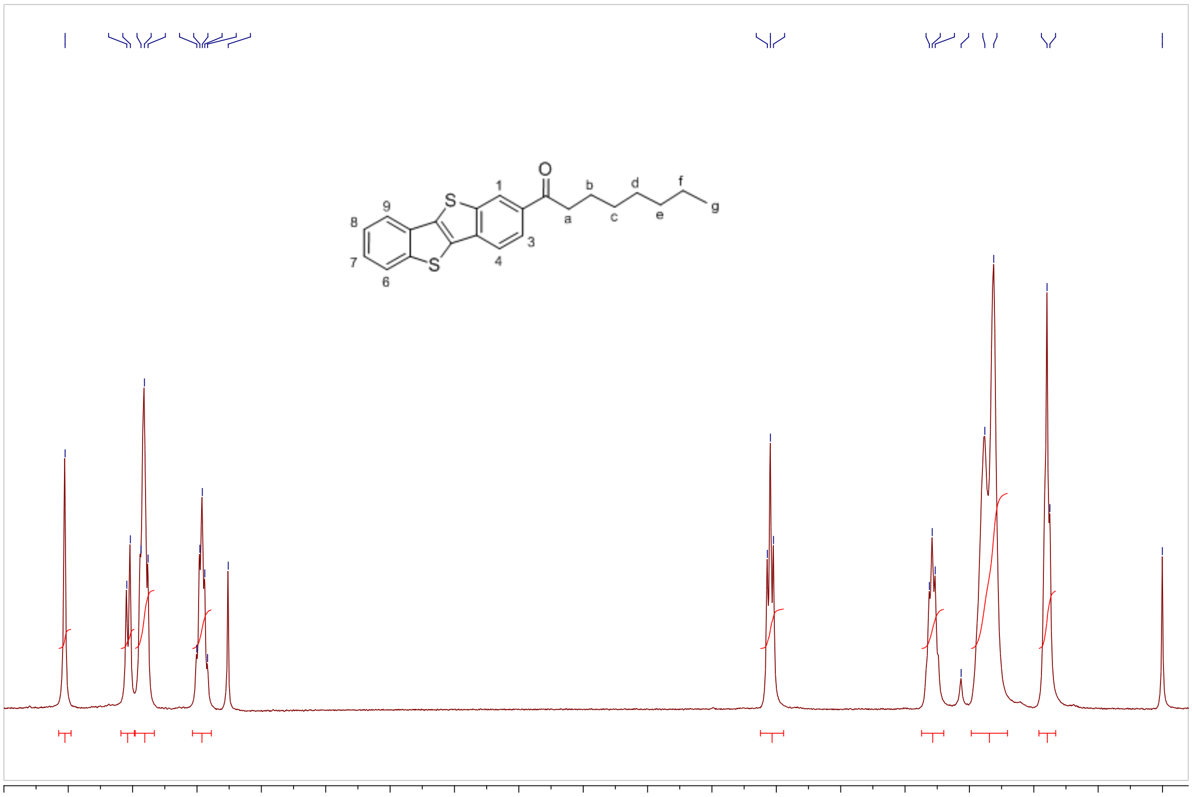


Figure. S4. ^{13}C NMR spectra of **8** in $CDCl_3$ (25°C)

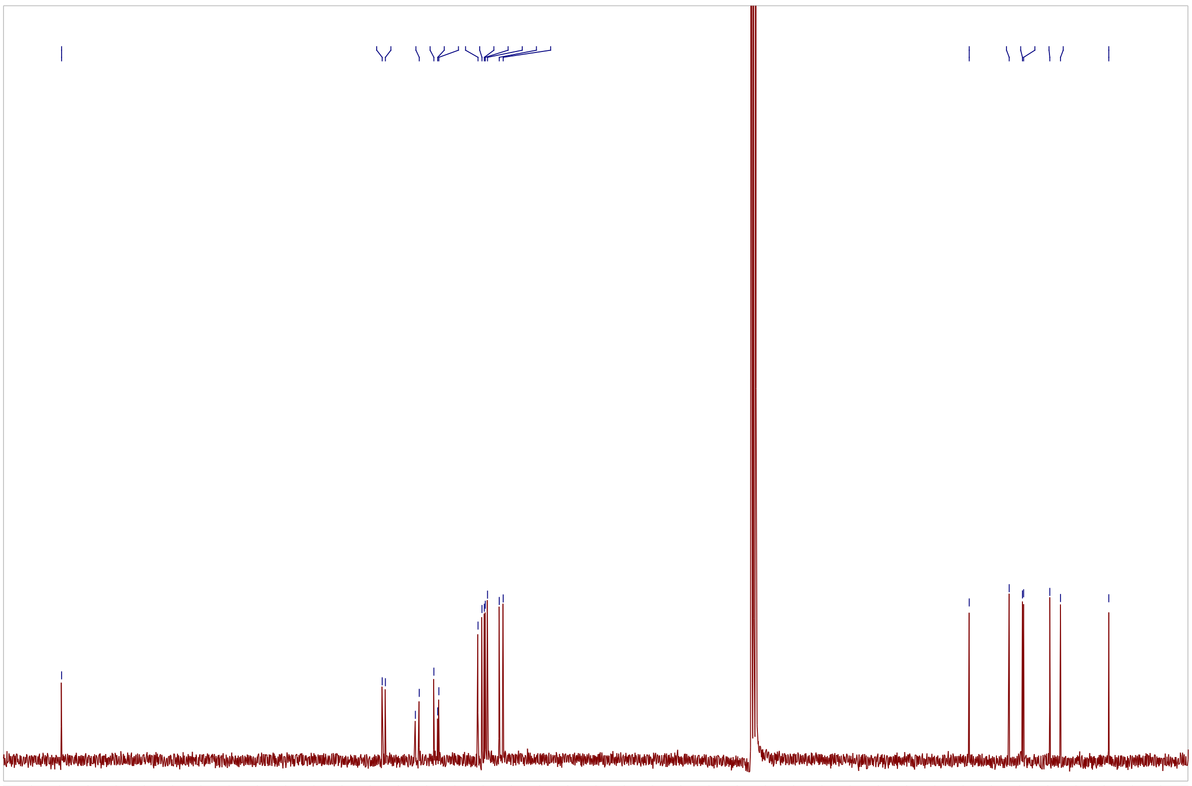


Figure. S5. ^{1}H NMR spectra of **9** in $CDCl_3$ (25°C)

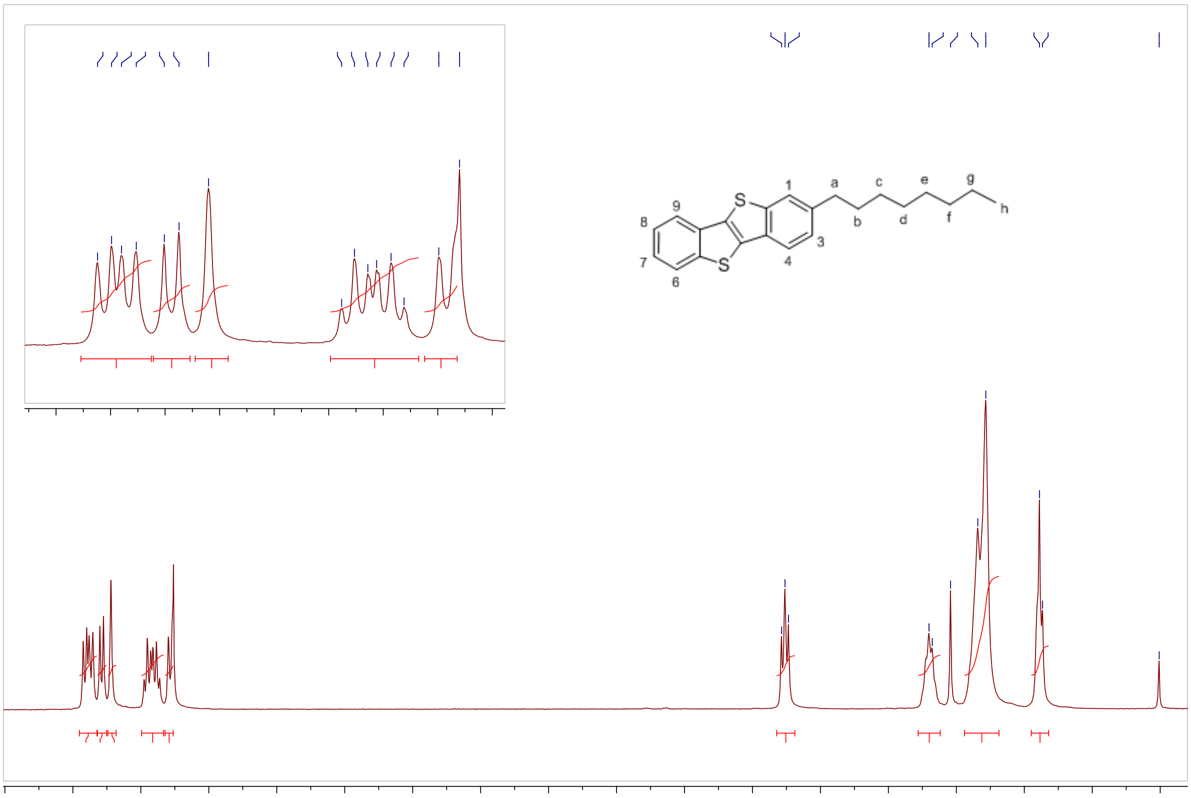


Figure. S6. ^{13}C NMR spectra of **9** in $CDCl_3$ (25°C)

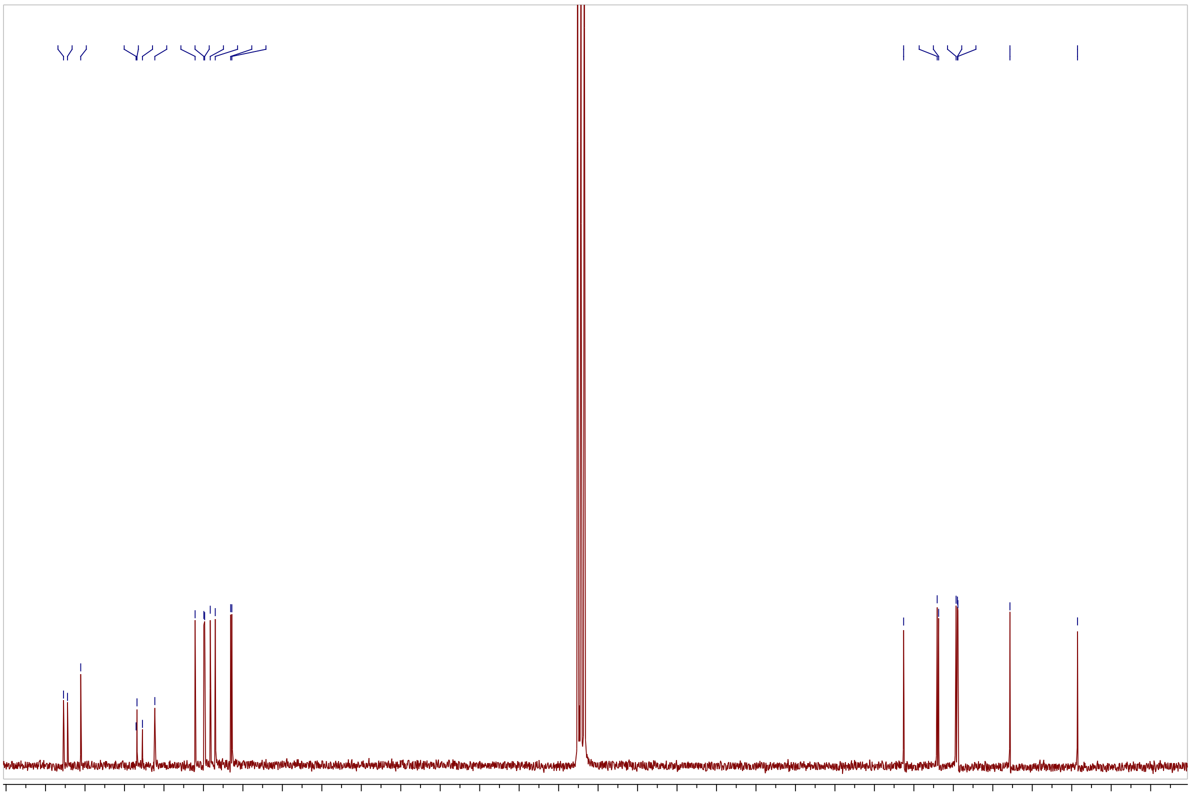


Figure. S7. ^{1}H NMR spectra of **10** in $CDCl_3$ (25°C)

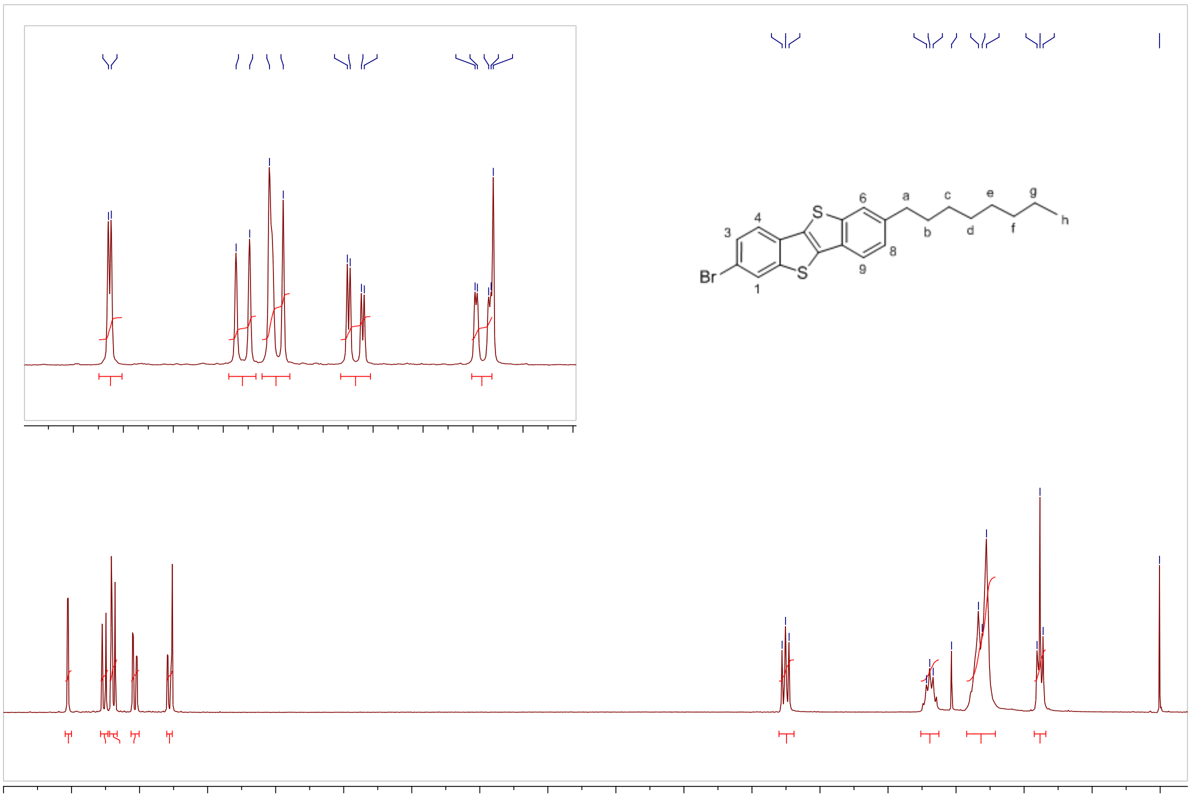


Figure. S8. ^{13}C NMR spectra of **10** in $CDCl_3$ (25°C)

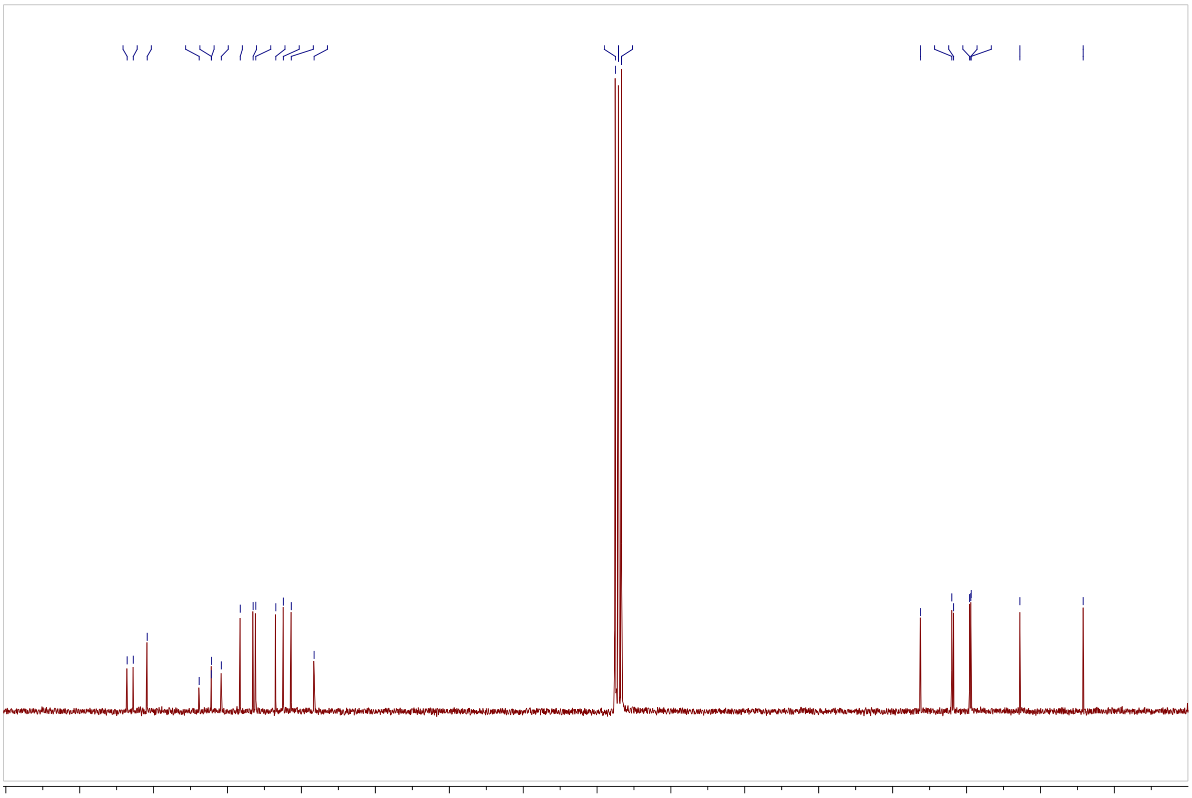


Figure. S9. ^{1}H NMR spectra of **4b** in $C_2D_2Cl_4$ (100°C)

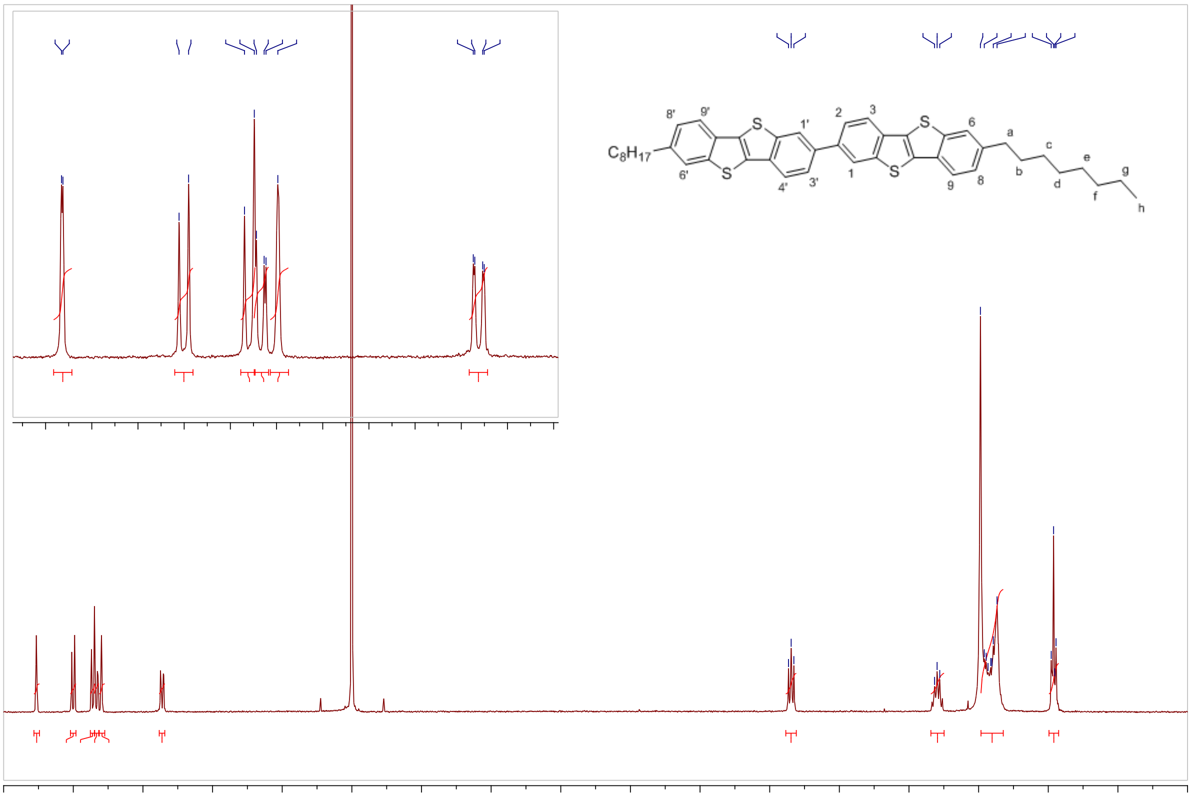
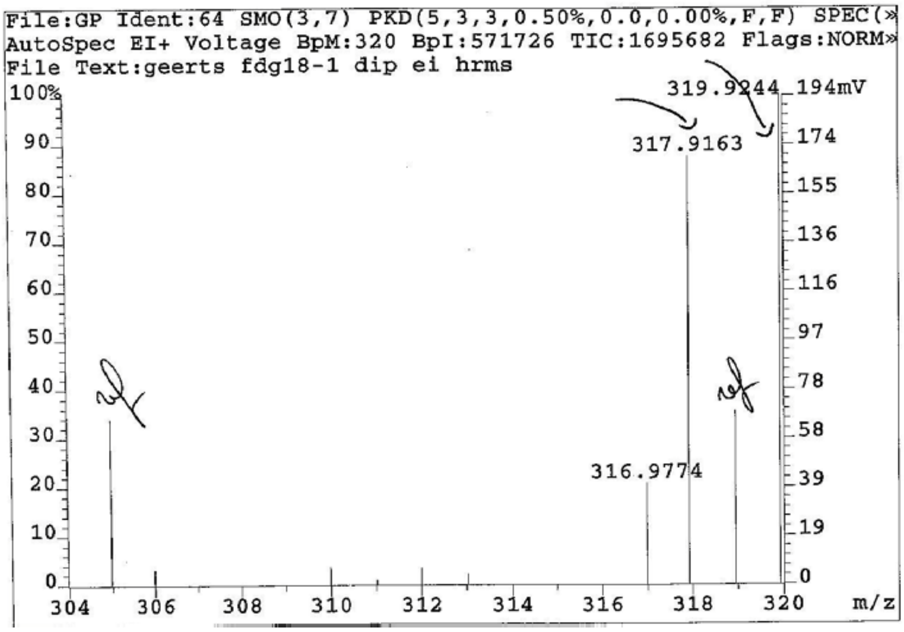


Figure S10. High resolution EI mass spectrum of **7**



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317.916299	50.0			20.0	200	400	1	2	2	1	1
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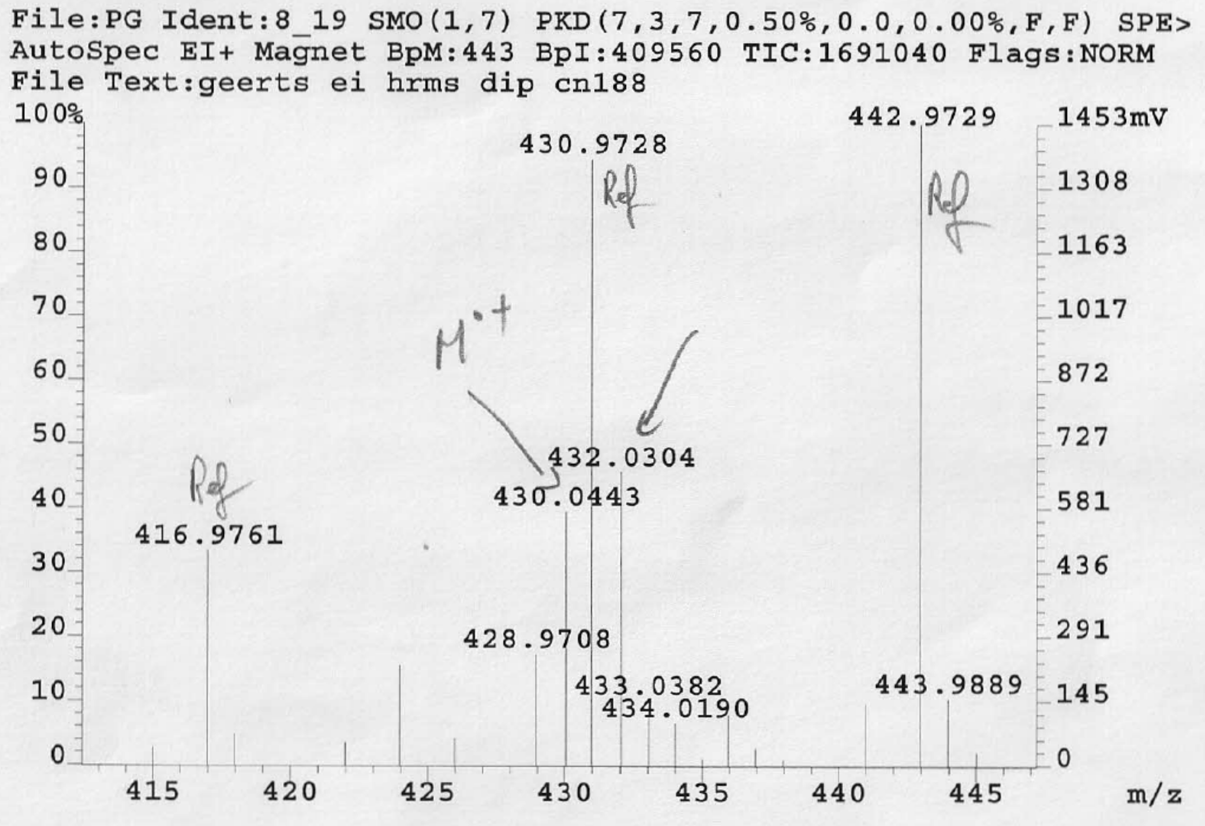
	-7.6	-2.4	317.913883	16.0	17	3			1	1	
	8.7	2.8	317.919064	16.5	16	1	1	2		1	
	-13.7	-4.4	317.911949	2.5	6	9	1	2	2		1
	-14.7	-4.7	317.911628	1.0	7	12		1		1	1
	15.3	4.9	317.921153	7.0	10	7		2	1		1
	19.3	6.1	317.922436	11.5	13	5	1	2	1	1	
	-24.3	-7.7	317.908577	7.5	9	5	1	2	1		1
	25.9	8.2	317.924525	2.0	7	11		2	2		1
	29.9	9.5	317.925808	6.5	10	9	1	2	2	1	
	-34.9	-11.1	317.905205	12.5	12	1	1	2			1
	-36.6	-11.6	317.904679	11.5	13	5	1		2	1	
	-40.6	-12.9	317.903396	7.0	10	7			2		1
	-47.2	-15.0	317.901307	16.5	16	1	1		1	1	
	48.3	15.3	317.931641	16.0	17	3		2		1	

Figure S11. High resolution EI mass spectrum of **10**



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File Text:geerts ei hrms dip cn188

Heteroatom Max: 20 Ion: Both Even and Odd

Limits:

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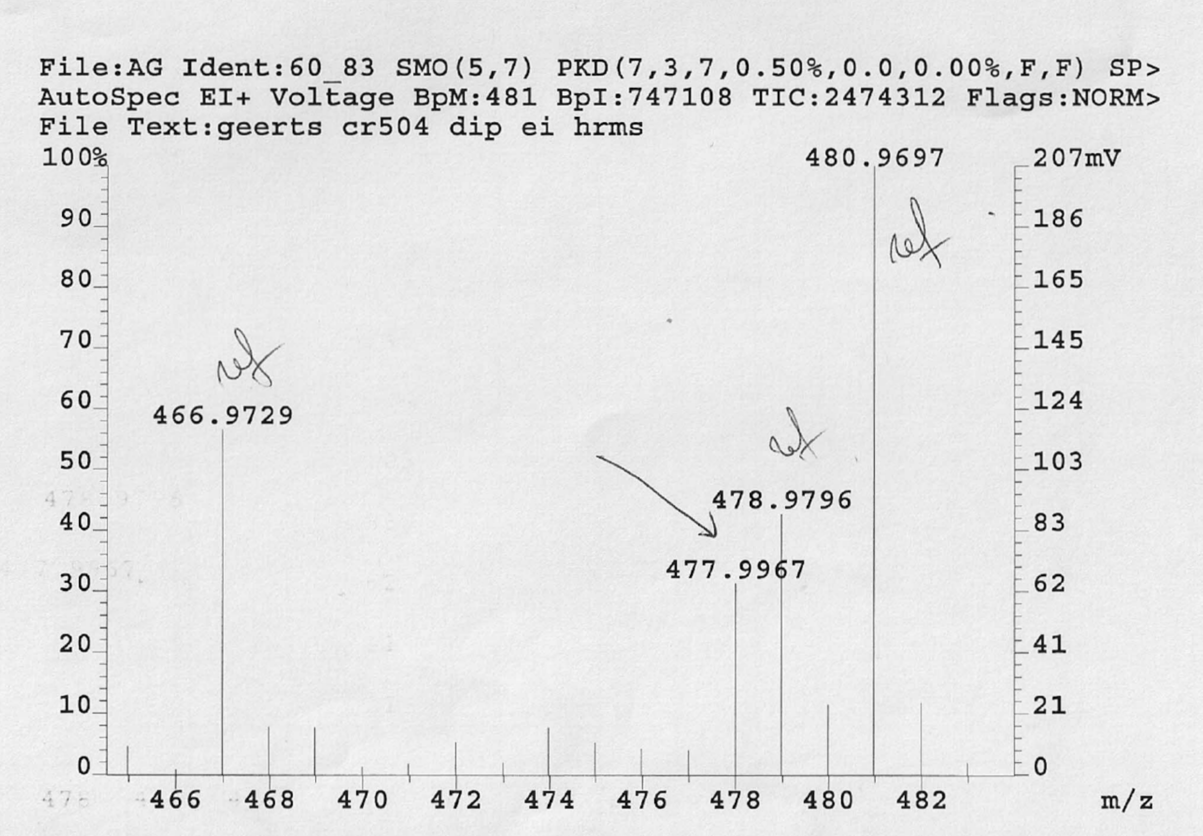
430.044323	50.0			20.0	200	400	2	1
Mass	PPM	mDa	Calc. Mass	DBE	C	H	S	Br
430.044323	-4.3	-1.9	430.042456	11.0	22	23	2	1

Figure. S12. High resolution EI mass spectrum of **4a**



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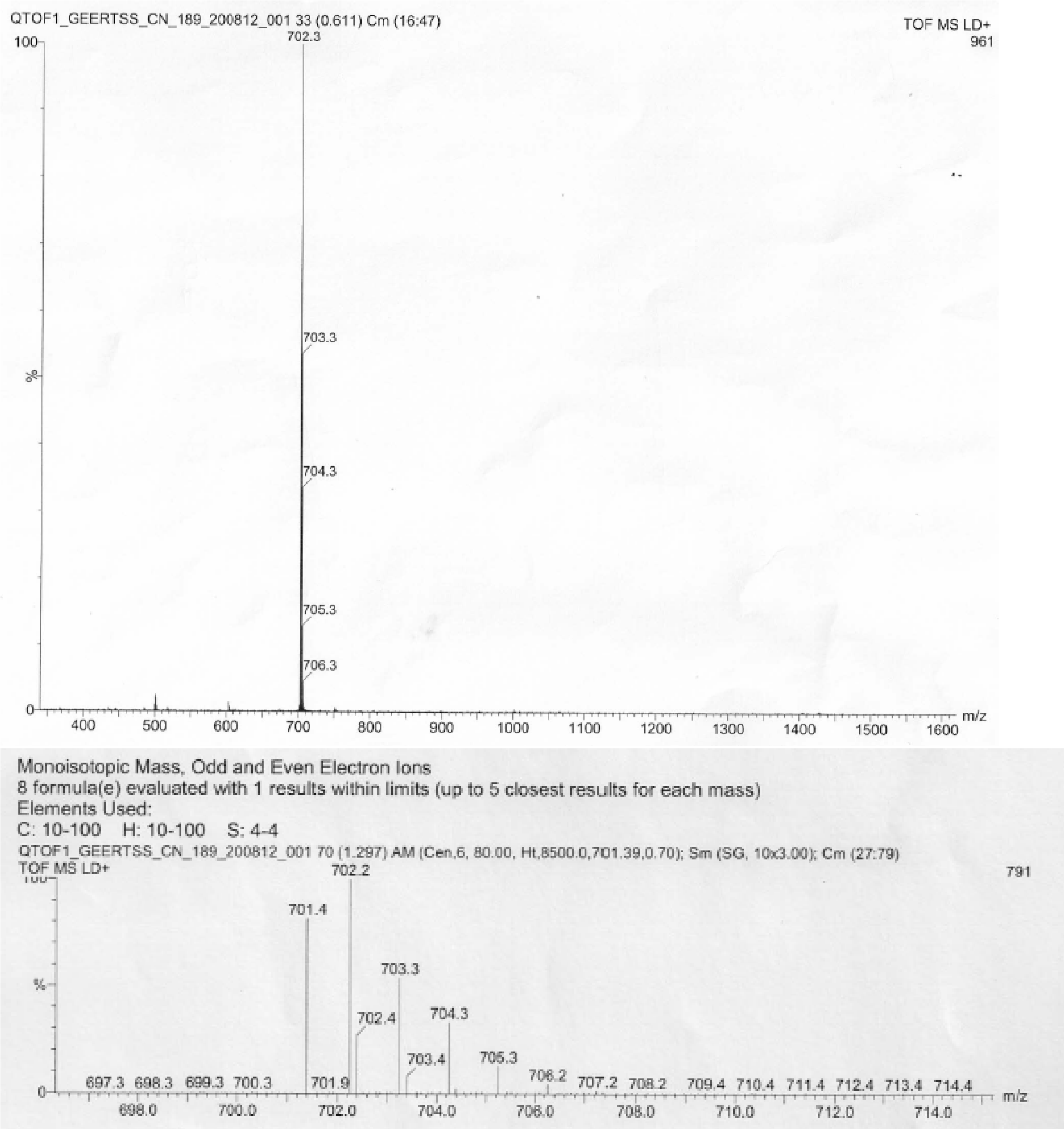
Heteroatom Max: 20 Ion: Both Even and Odd

Limits:

				-0.5	0	0	4
477.995831		50.0		50.0	200	400	4
Mass	PPM	mDa	Calc. Mass	DBE	C	H	S
477.995831	4.2	2.0	477.997838	22.0	28	14	4

Figure. S13. High resolution MALDI mass spectrum of **4b**



Minimum:				-5.0		
Maximum:		100.0	100.0	100.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
702.2489	702.2482	0.7	1.0	22.0	0.3	C44 H46 S4

UV-Vis and Fluorescence spectra

Absorption spectra of toluene solutions of **1a**, **9**, **4a**, **4b** were recorded on an Agilent 8453 spectrophotometer in a quartz cell (optical path of 1 cm) in toluene (concentration solutions of 10^{-5}M were used). Thin films of **1a**, **4a**, and **4b** were prepared on sapphire using shearing (**1a**) and on glass slides using thermal evaporation (**4a** and **4b**). Absorption spectra of thin films of **1a**, **4a**, and **4b** were recorded using Agilent Cary 6000i UV/Vis/NIR spectrophotometer. Emission spectra of toluene solutions of **4a** and **4b** were measured on an Aminco Bowman series 2 luminescence spectrophotometer. Measurements have been done at room temperature.

Figure S14: Absorption spectra of toluene solutions (~ 10^{-5}M) of **1a** (red), **9** (black), **4a** (green), and **4b** (blue). The difference of λ_{max} between 4a and 4b is assigned to different torsion angles between BTBT units.

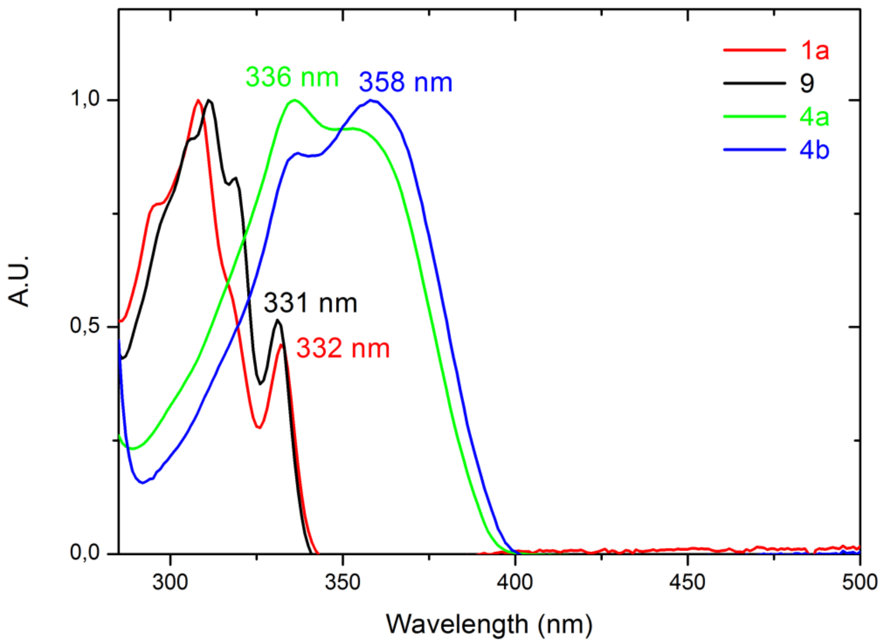


Figure S15: Absorption spectra of thin films of **1a**, **4a**, and **4b** prepared on sapphire using shearing (**1a**) and deposited on glass slides by thermal evaporation (**4a** and **4b**)

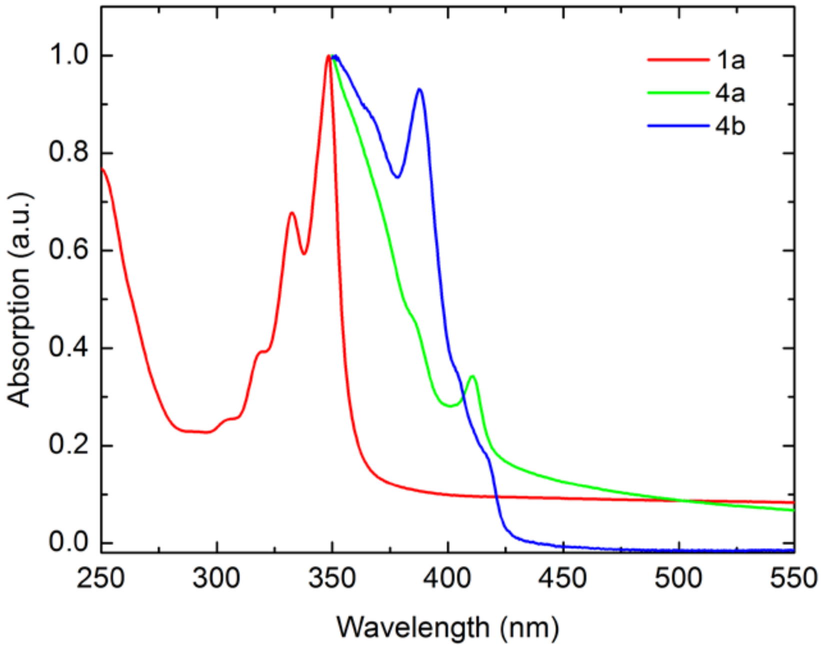
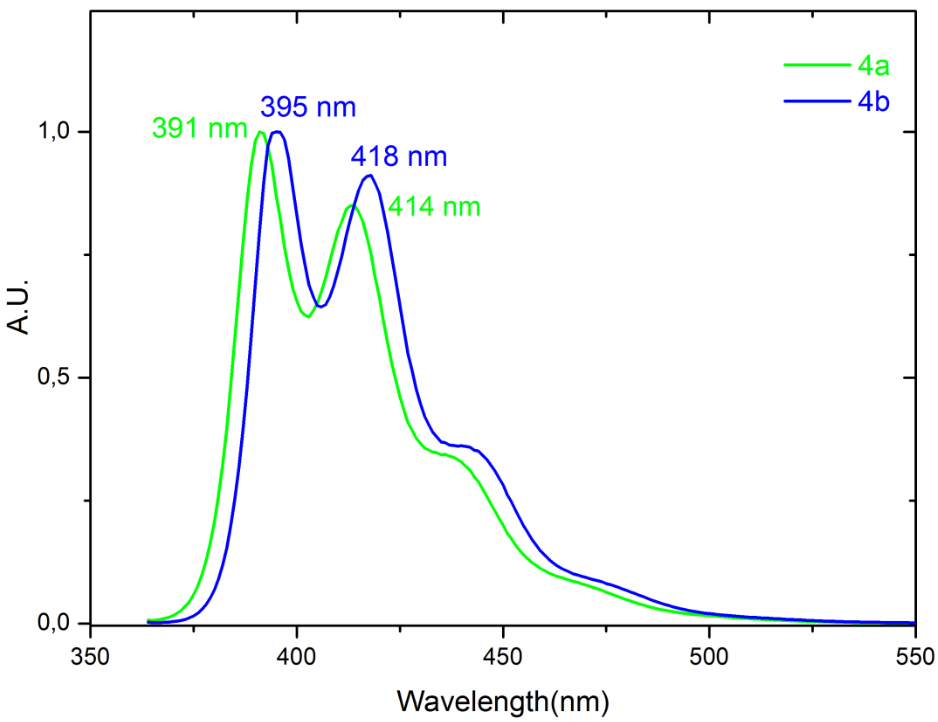


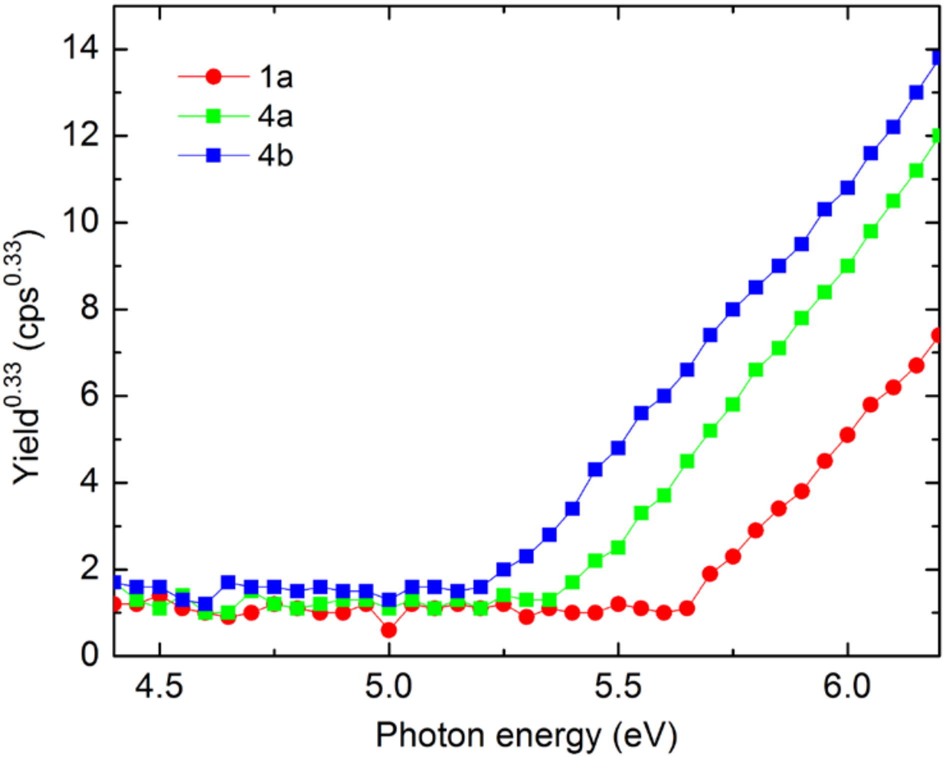
Figure S16: Fluorescence spectra of 10^{-5}M toluene solutions of **4a** (green) and **4b** (blue)



PESA spectra

Thin films of **1a**, **4a**, and **4b** were prepared on sapphire using shearing (**1a**) and on glass slides through thermal evaporation (**4a** and **4b**). Photoelectron spectroscopy in air (PESA) spectra of thin films of **1a**, **4a**, and **4b** were recorded using Riken Keiki photoelectron spectrometer in air (model AC-2)

Figure S17: PESA spectra of thin films of **1a**, **4a**, and **4b** deposited on sapphire by shearing (**1a**) and on glass slides by thermal evaporation (**4a** and **4b**).



TFT characteristics

Table S1: Summary of data for TFTs

Compound	Gate dielectric	T_{dep} [°C]	μ_{sat} [$cm^2 V^{-1}s^{-1}$]	I_{on}/I_{off}	V_T [V]
4a	SiO_2 (300nm)	25	0.0069 ± 0.0007	$(1.8 \pm 1.7) \times 10^4$	-(20 ± 5)
		60	0.025 ± 0.001	$(4.0 \pm 4.4) \times 10^4$	-(17 ± 1)
		90	0.043 ± 0.003	$(4.6 \pm 4.1) \times 10^4$	-(4.2 ± 2.0)
		120	0.094 ± 0.009	$(7.5 \pm 11.5) \times 10^5$	-(31 ± 1)
	BCB (50nm)	25	0.038 ± 0.003	$(1.3 \pm 0.7) \times 10^5$	-(28 ± 2)
	on	60	0.16 ± 0.01	$(7.9 \pm 6.8) \times 10^5$	-(20 ± 1)
	SiO_2 (300nm)	90	0.29 ± 0.02	$(5.4 \pm 5.4) \times 10^5$	-(18 ± 1)
		120	0.29 ± 0.04	$(4.3 \pm 1.2) \times 10^4$	-(36 ± 4)
	OTS-treated	25	0.085 ± 0.009	$(1.5 \pm 3.6) \times 10^7$	-(21 ± 1)
	SiO2 (300nm)	60	0.39 ± 0.01	$(3.7 \pm 3.3) \times 10^7$	-(14 ± 2)
		90	0.41 ± 0.05	$(3.6 \pm 2.8) \times 10^6$	-(10 ± 2)
		120	0.67 ± 0.12	$(2.9 \pm 0.8) \times 10^5$	-(23 ± 3)
4b	SiO_2 (300nm)	25	0.0019 ± 0.0001	$(3.1 \pm 1.1) \times 10^5$	-(30 ± 7)
		60	0.15 ± 0.02	$(1.1 \pm 0.4) \times 10^5$	-(12 ± 3)
		90	0.31 ± 0.01	$(6.5 \pm 6.0) \times 10^5$	-(18 ± 1)
		120	0.29 ± 0.01	$(2.0 \pm 0.6) \times 10^4$	5.0 ± 2.5
	BCB (50nm)	25	0.010 ± 0.001	$(7.1 \pm 0.2) \times 10^3$	-(42 ± 3)
	on	60	0.18 ± 0.01	$(4.7 \pm 3.9) \times 10^5$	-(19 ± 2)
	SiO_2 (300nm)	90	0.33 ± 0.03	$(2.5 \pm 0.9) \times 10^5$	-(29 ± 3)
		120	0.53 ± 0.01	$(1.7 \pm 0.3) \times 10^5$	-(14 ± 2)
	OTS-treated	25	0.34 ± 0.04	$(2.9 \pm 1.2) \times 10^5$	-(33 ± 1)
	SiO2 (300nm)	60	1.33 ± 0.09	$(7.9 \pm 3.1) \times 10^5$	-(25 ± 1)
		90	1.17 ± 0.09	$(1.4 \pm 3.2) \times 10^6$	-(29 ± 1)
		120	0.15 ± 0.02	$(1.5 \pm 1.2) \times 10^6$	-(17 ± 3)

T_{dep} is the substrate temperature during the deposition of thin-films. μ_{sat} is the mobility value in saturation region. All the measurements were done in air under dark condition.

Thin-film morphologies

Figure S18: AFM height images of thin films of **4a** on three kinds of dielectric. The nominal thicknesses of all the films were 40nm. The substrate temperature during deposition was 120°C, at which we have obtained the highest mobility for **4a**. The sizes of all the images were 5μm×5μm.

(a) On SiO_2 (300nm) (b) On BCB (50nm) on SiO_2 (300nm) (c) On OTS-treated SiO_2 (300nm)

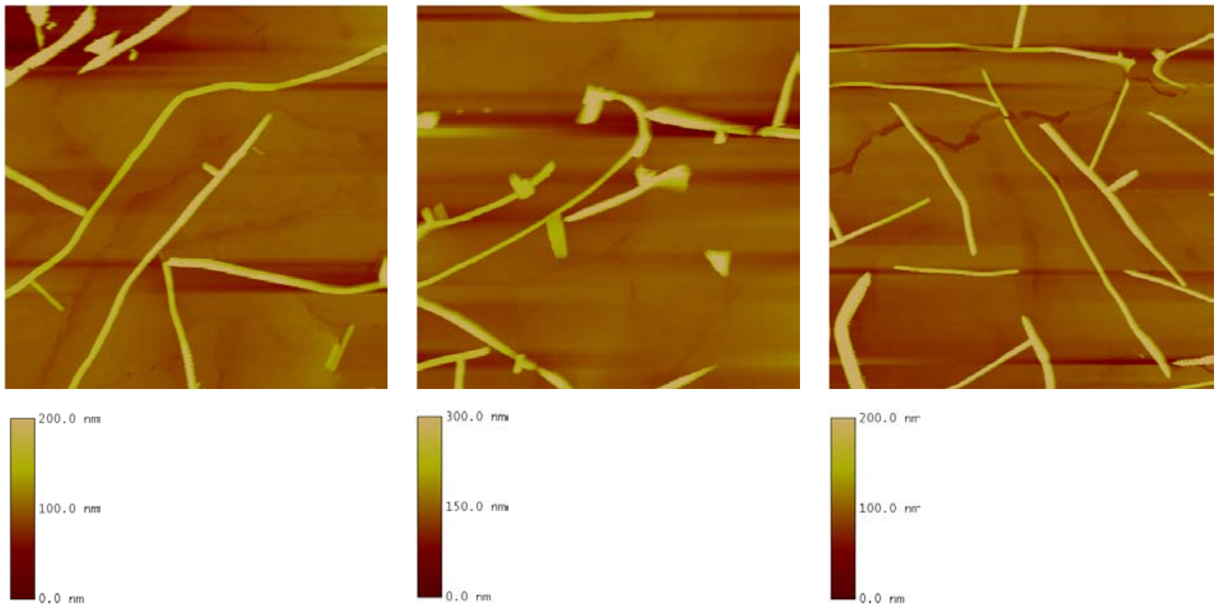


Figure S19: AFM height images of thin films of **4b** on three kinds of dielectric. The nominal thicknesses of all the films were 40nm. The substrate temperature during deposition was 60°C, at which we have obtained the highest mobility for **4b**. The sizes of all the images were 5μm×5μm.

(a) On SiO_2 (300nm) (b) On BCB (50nm) on SiO_2 (300nm) (c) On OTS-treated SiO_2 (300nm)

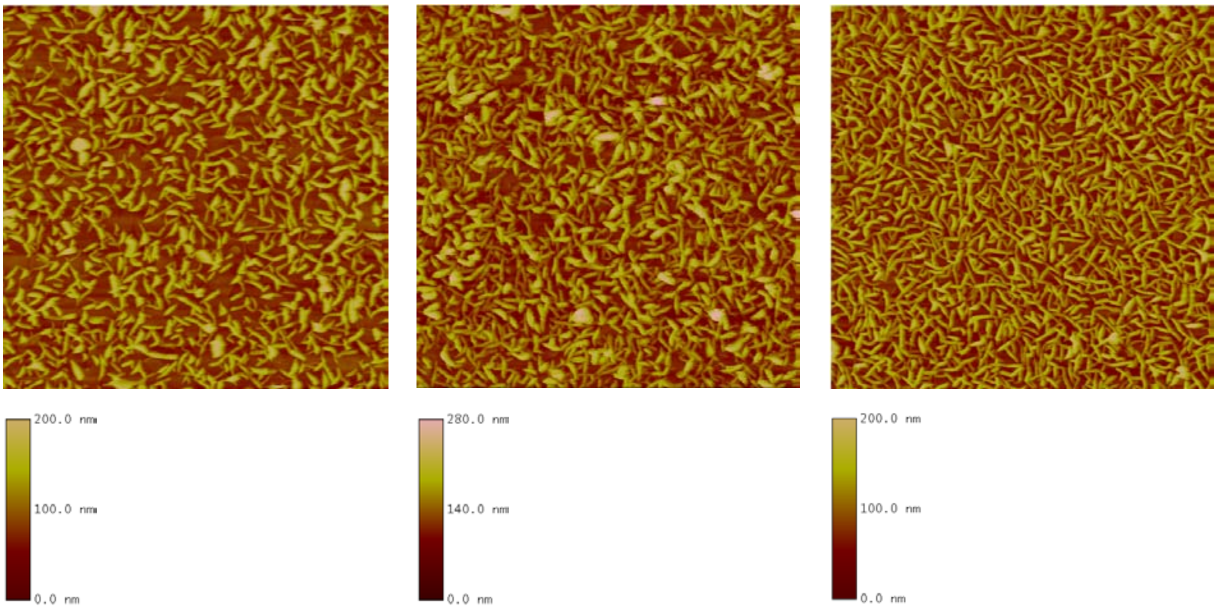


Figure S20: AFM height images of thin films of **4a** with various nominal thicknesses (1-40nm) grown on OTS-treated SiO_2. The substrate temperature during deposition was 60°C. All the images were 2μm×2μm images.

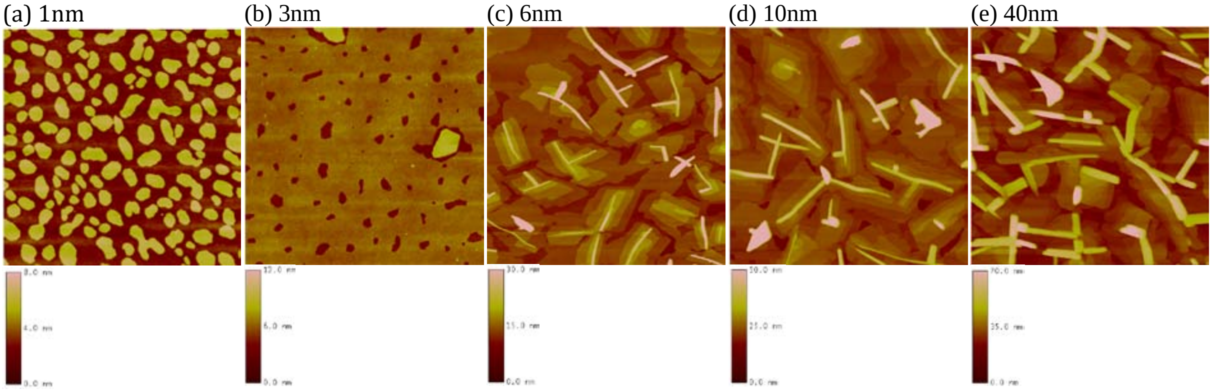


Figure S21: AFM phase images of thin films of **4b** with various nominal thicknesses (1-40nm) grown on OTS-treated SiO_2. The substrate temperature during deposition was 60°C. All the images were 1μm×1μm images.

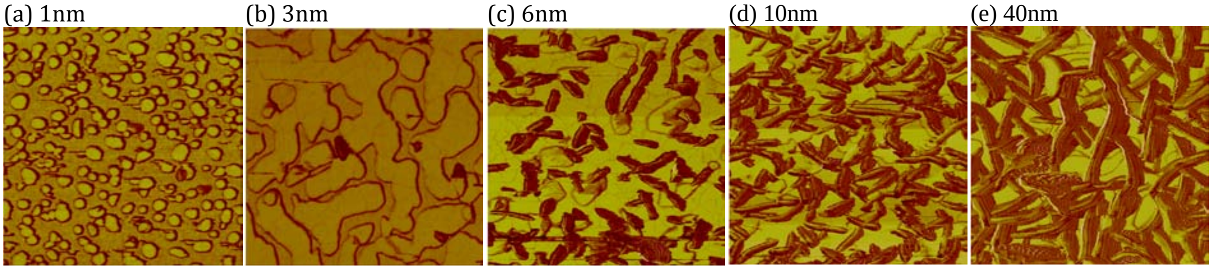
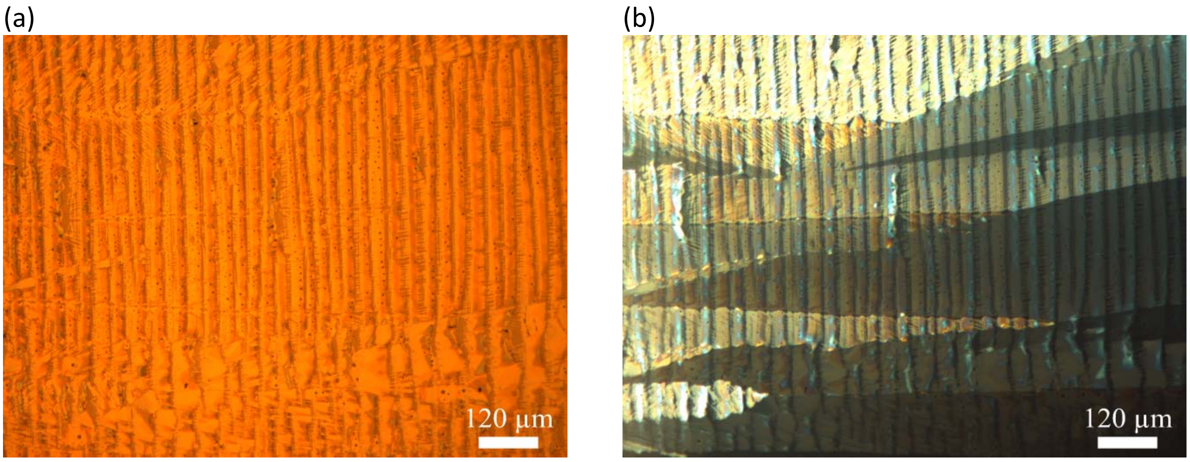


Figure S22: (a) optical micrograph and (b) cross-polarized optical micrograph of solution-sheared thin films of **1a**



Grazing incidence X-ray diffraction (GIXD) of thin films

Figure S23: Grazing incidence X-ray diffraction (GIXD) images of thin films (40nm) of **4a** (a-c) and **4b** (d-g) for various T_{dep}. The diffraction peaks indicated by orange arrows were not used to calculate lattice constants.

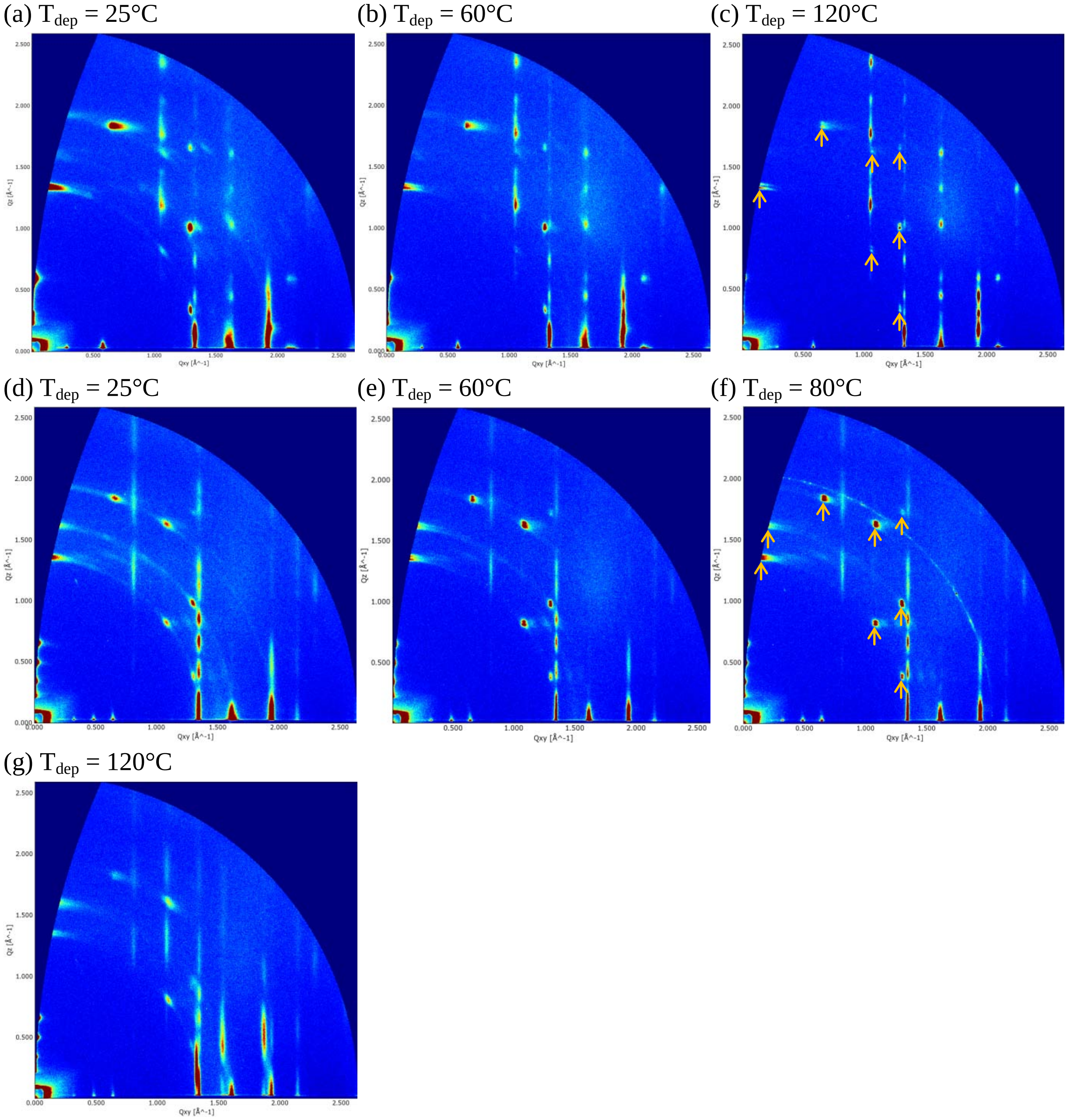


Table S2: Lattice parameters of thin films (40nm) of **4a** and **4b** as determined from GIXD data.

	4a			**4b**
	This work	Yu et al.[1] (Phase A)	Yu et al.[1] (Phase A*)	This work
T_{sub}	120°C	N/A	N/A	80°C
a (Å)	6.00	6.10	5.88	5.86
b (Å)	7.74	7.82	8.08	7.81
c (Å)	23.37	N/A	N/A	40.31
α (°)	88.01	N/A	N/A	88.33
β (°)	84.73	N/A	N/A	88.57
γ (°)	89.96	N/A	N/A	90.09
V (Å^3)	1080	N/A	N/A	1845
d(001)	23.25	21.86	21.86	40.28

[1] H. Yu, W. Li, H. Tian, H. Wang, D. Yan, J. Zhang, Y. Geng and F. Wang, *ACS Appl. Mater. Interfaces*, 2014, 6, 5255-5262.

Figure S24: Coherence lengths of thin films (40nm) of **4a** and **4b**. The coherence lengths were calculated from full width at half maximum (FWHM) of GIXD peaks using Scherrer's equation. (111) diffraction (Q_{xy}=1.3233-1.3252Å^{-1} and Q_z=0.1460-0.1532Å^{-1}) was used to calculate the coherence lengths of **4a**. ($\bar{1}\bar{1}4$) diffraction (Q_{xy}=1.3403-1.3418Å^{-1} and Q_z=0.6628-0.6717Å^{-1}) was used for the coherence length calculations of **4b**.