Supplementary Material (ESI) for Journal of Materials Chemistry

ELECTRONIC SUPPLEMENTARY INFORMATION

Room-Temperature Discotic Liquid-Crystalline Coronene Diimides Exhibiting High Charge-Carrier Mobility in Air

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1. Isomeric Composition of Perylene and Coronene Diimide Derivatives

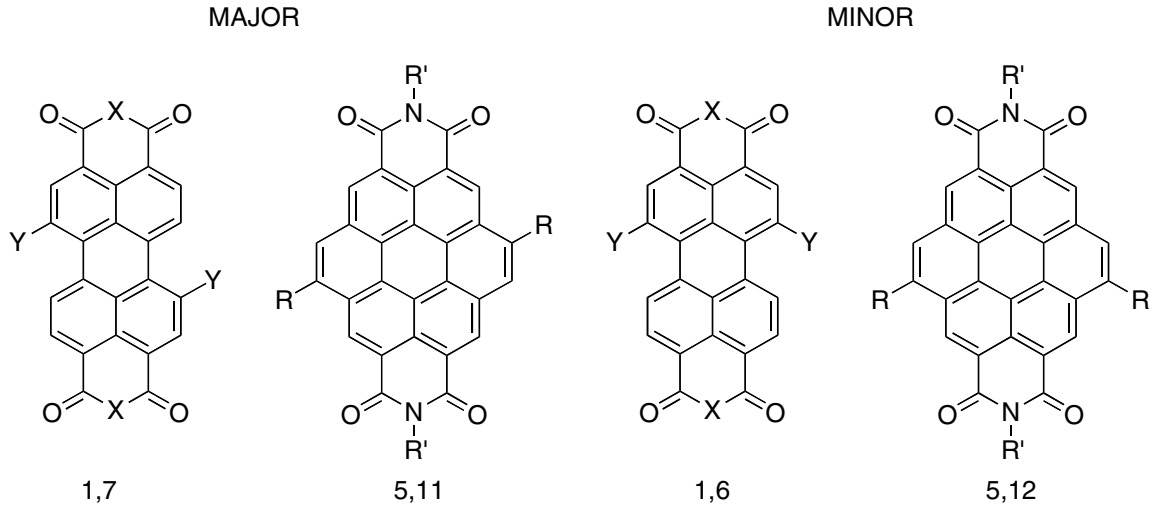


Figure S1. Isomers of perylene diimide and coronene diimides.

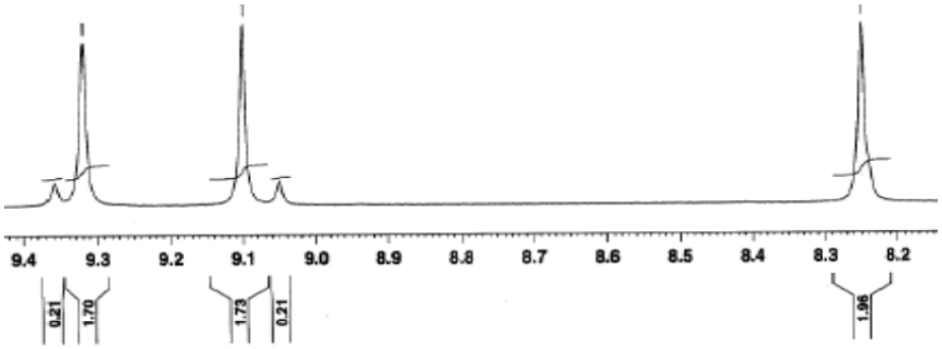


Figure S2. Aromatic region of the ^{1}H NMR spectrum of **3** showing the presence of 5,11- and 5,12-isomers.

2. Absorption and Emission Spectra for Coronene Diimides

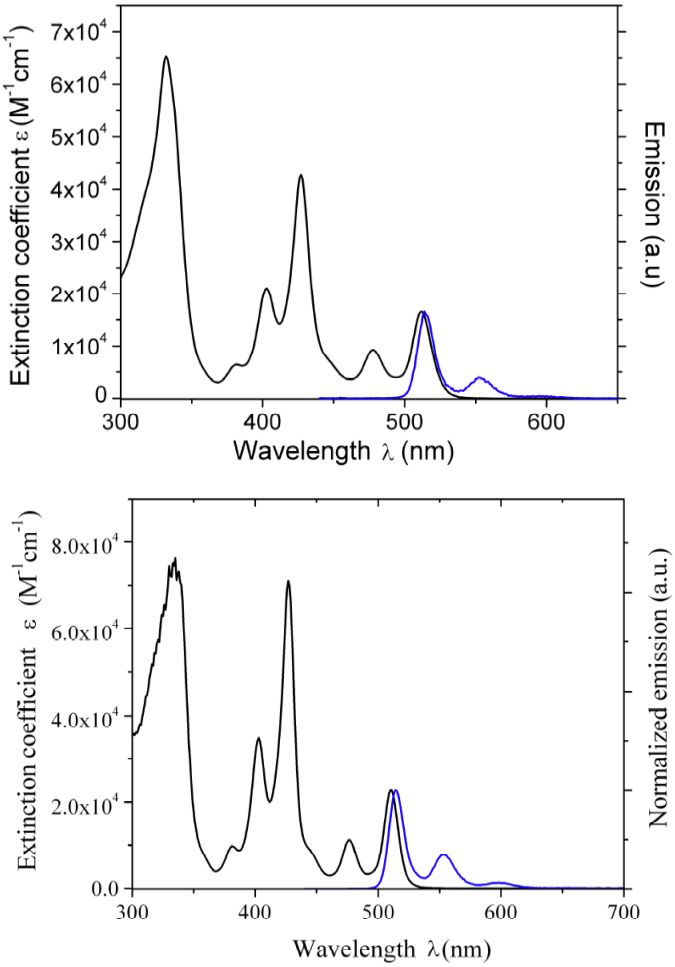


Figure S3. Absorption and emission for **2b** (above) and **3** (below) in dichloromethane. Excitation wavelength is 427 nm.

Table S1. Absorption and Emission Data for Coronene Diimides in Dichloromethane.

	lowest energy $\lambda_{max\text{-}fl}$ / nm (ε_{max} / $M^{-1}cm^{-1}$)	$\lambda_{max\text{-}fl}$ / nm	Φ_{fl}[a]
1a	512 (20700)	516	0.01
1b	512 (20300)	516	0.01
1c	512 (18500)	516	0.01
2a	508	511	0.16
2b	512 (16500)	514	0.06
3	510(22800)	514	0.23

[a]Fuorescence quantum yield, determined using an excitation wavelength of 400 nm and perylene as a standard.

3. Aggregation Behaviour of Coronene Diimides

The aggregation behaviour of **1a-c** and **3** was studied by absorption spectroscopy in methylcyclohexane. Upon increasing the concentration, the absorption properties of the coronene diimides experience significant changes with certain defined isosbestic points (Figure S4a). The spectra seen at higher concentrations resemble those of the solid-state thin films (shown in Figure S5 for **1b**). These marked spectral changes strongly suggest formation of *J*-type aggregates[1-4] in methycyclohexane at higher concentrations as well as in solid state.

There are several models for studying self-association processes, among which the simplest one is the equal-K model[5] in which it is assumed that the constant for each molecule adding to a growing stack is the same and that the molecules within the same stack have the same properties. The fraction of the free molecules at certain concentrations is determined by equation:

$$\alpha = \frac{2KC + 1 - \sqrt{4KC + 1}}{2K^2C^2} \qquad \text{(Eq. S1)}$$

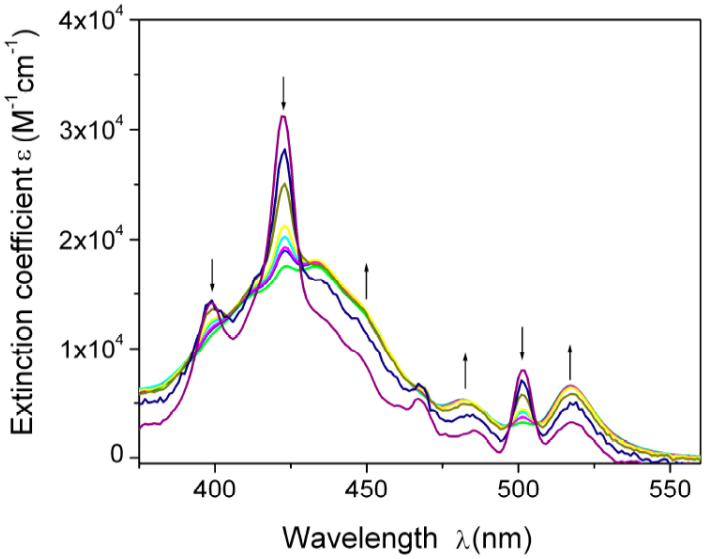
where K is the formation constant of the aggregate and C is the total concentration of the molecules (free molecules and aggregated molecules).

For UV-vis studies, in combination with Beer's Law, one can derive from Eq S1:

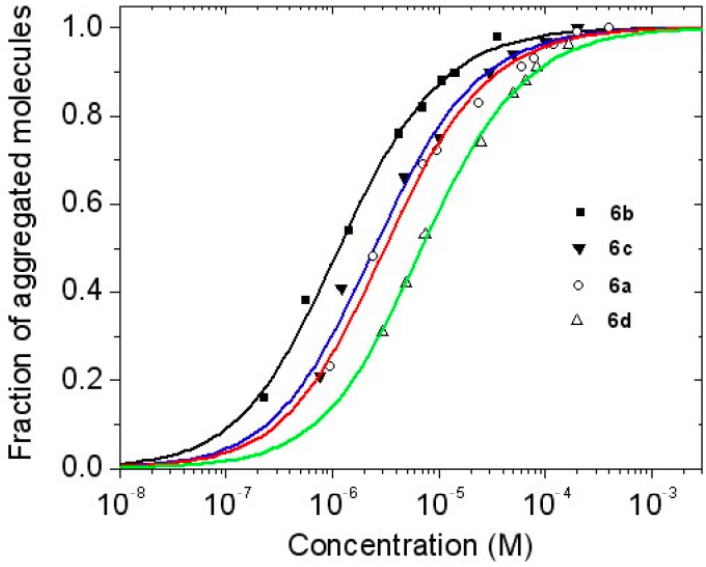
$$\varepsilon(C) = \frac{2KC + 1 - \sqrt{4KC + 1}}{2K^2C^2}(\varepsilon_f - \varepsilon_a) + \varepsilon_a \qquad \text{(Eq. S2)}$$

where $\varepsilon(C)$ is the observed extinction coefficient at certain concentration, ε_f is the extinction coefficient of the free molecules and ε_a is the extinction coefficient of the aggregated molecules in the stacks. This method has been used to study the solution aggregation behavior of perylene derivatives.[3,6,7]

All of the four coronene diimides show similar aggregation behaviours that were modeled using equation S2 by nonlinear least square regression fitting (Figure S4b). The aggregating ability of the four compounds decreases in the order of **1b, 1c**, **1a** and **3**, with aggregation constants of 5.1×10^5, 2.4×10^5, 1.9×10^5 and 0.8×10^5 M^{-1}, respectively.



(a)



(b)

Figure S4. (a) Absorptivity for different concentrations (range: 2.29×10^{-7} M to 3.57×10^{-5} M) of **1b** in methylcyclohexane. (b) Fraction present as aggregates as a function of concentration for coronene diimides in methylcyclohexane (calculated using absorptivity at 420 nm).

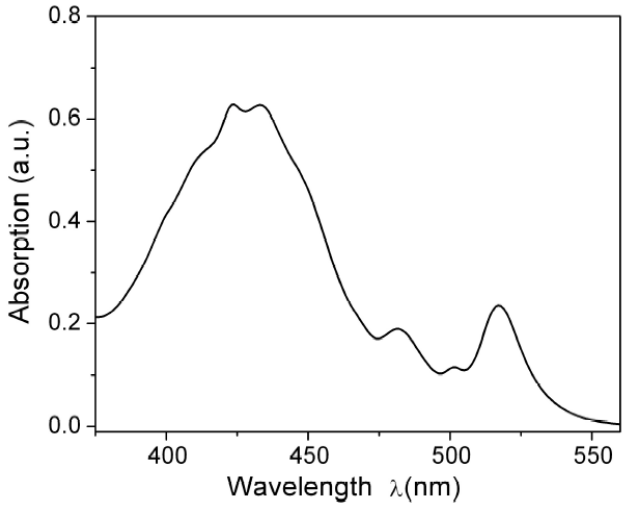


Figure S5. Absorption spectrum of a thin film of compound **1b** prepared by drop casting of a dichloromethane solution onto a quartz slide.

References for Aggregation Section

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4. Examples of Cyclic Voltammograms of Coronene Diimides

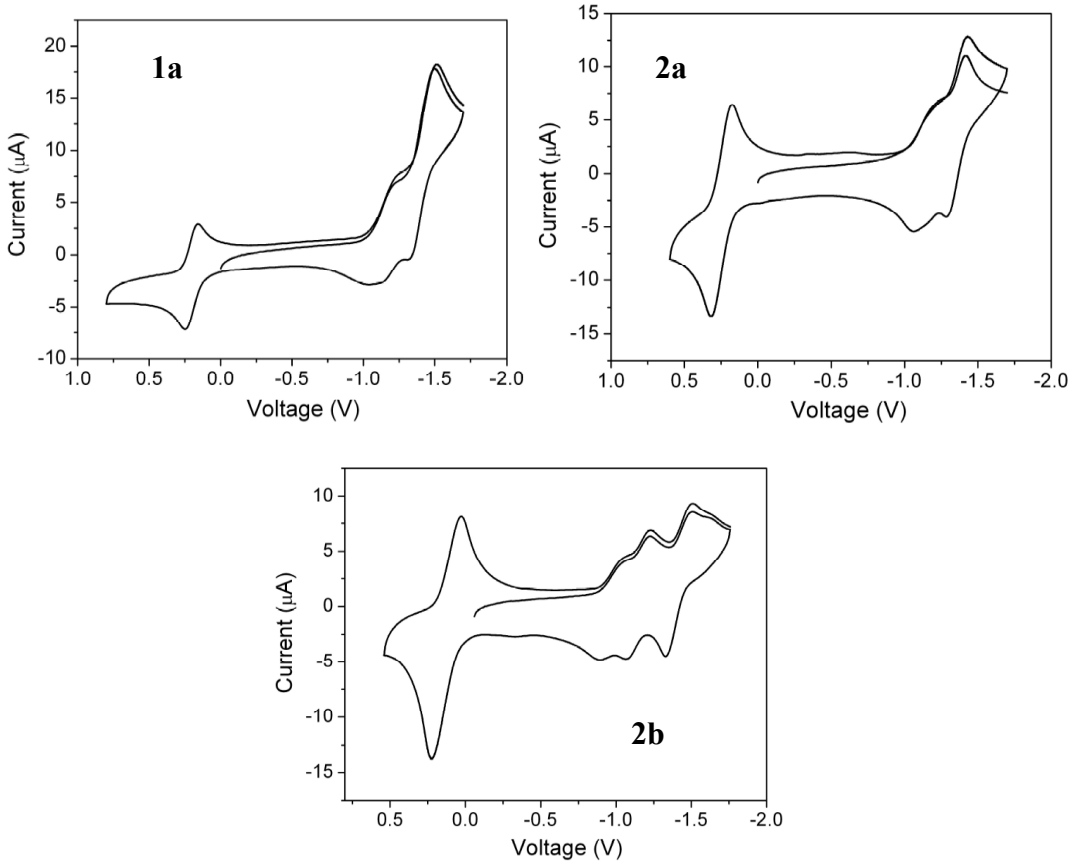

Figure S6. Cyclic voltammograms in 0.1 M Bu_4NPF_6 / dichloromethane solution with ferrocene (observed at ca. +0.2 V) as an internal standard recorded at a scan rate of 50 mVs^{-1}. The potential represented by the x-axis is relative to a AgCl/Ag pseudo-reference electrode.

5. Polarized Optical Microscopy.

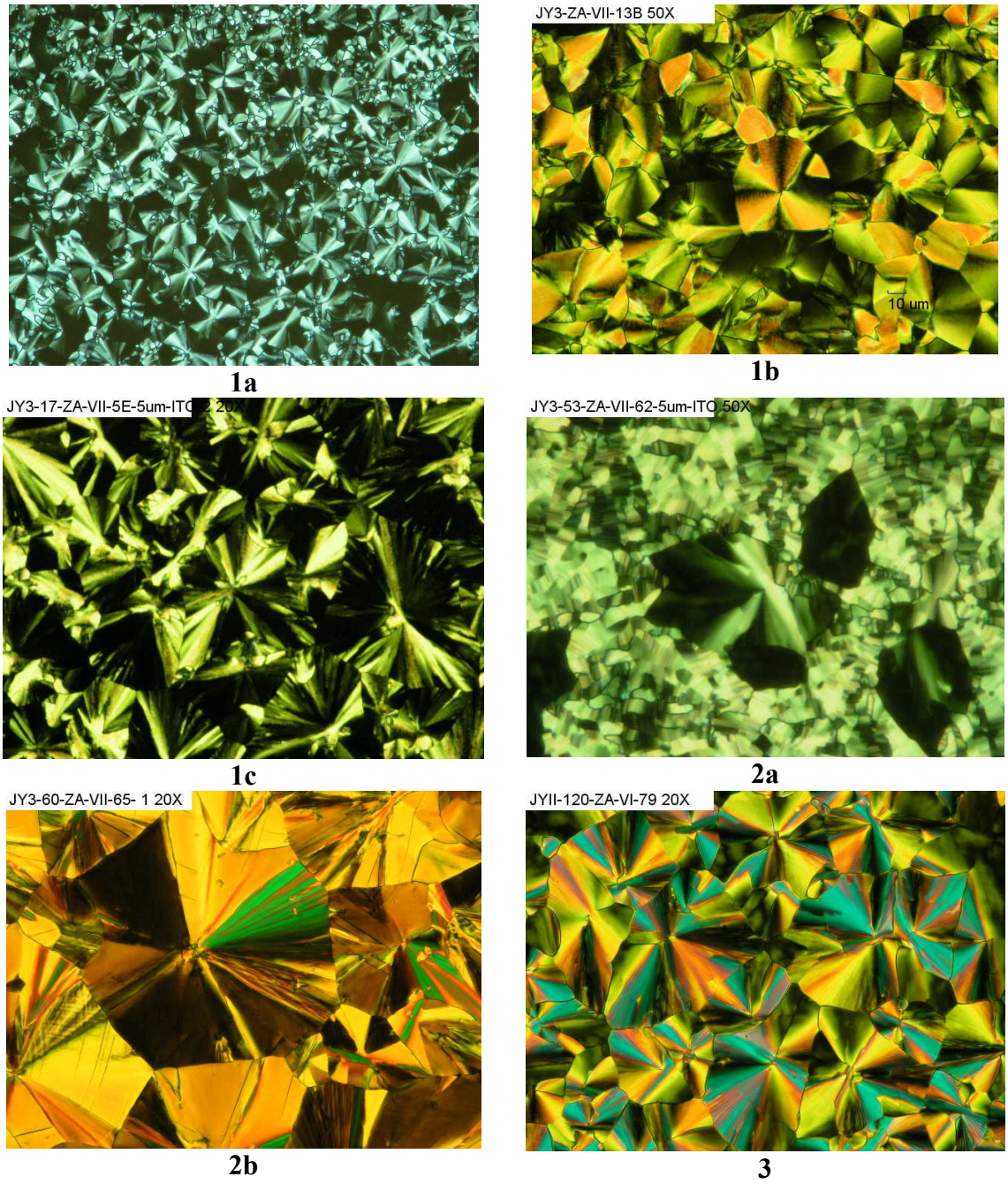

Figure S7. Optical textures between crossed polarizers of films of coronene diimides on glass cooled from the isotropic melt. Images sizes are 615 × 460 μm, except for **1b** and **2a**, for which the size is 250 × 190 μm.

6. X-ray Diffraction Data

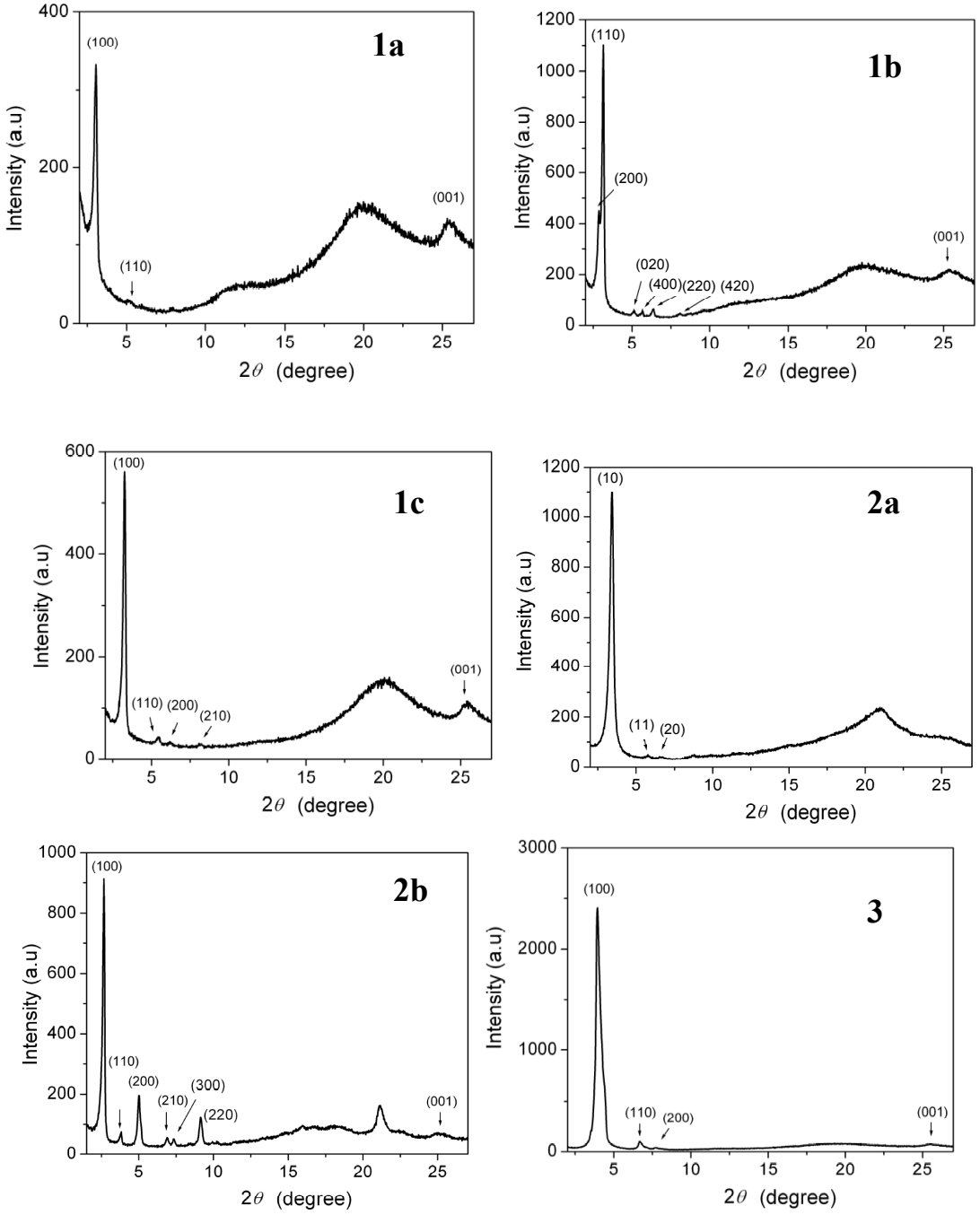

Figure S8. X-ray diffractograms for films of coronene diimides on glass at room temperature after cooling from the isotropic phase.

Table S2. Indexing of X-Ray Diffraction Data for Coronene Diimides (λ = 1.5406 Å).

Mesophase[a]	Index	2θ / °	*d* spacing / Å	Lattice parameters / Å
1a Col_h	(100)	3.05	28.94	$a_0 = 33.4$ $c_0 = 3.5$
	(110)	5.24	16.85	
	(001)	25.33	3.51	
1b Col_r	(200)	2.87	30.76	$a_0 = 61.6$ $b_0 = 34.4$ $c_0 = 3.5$
	(110)	3.15	28.03	
	(020)/(310)	5.13	17.21	
	(400)	5.68	15.55	
	(220)	6.40	13.80	
	(420)	8.10	10.91	
	(001)	25.39	3.51	
1c Col_h	(100)	3.25	27.16	$a_0 = 31.4$ $c_0 = 3.5$
	(110)	5.49	16.08	
	(200)	6.25	14.13	
	(210)	8.23	10.73	
	(001)	25.41	3.50	
2a Col_h	(10)	3.43	25.74	$a_0 = 29.7$
	(11)	5.75	15.36	
	(20)	6.60	13.38	
2b Col_h	(100)	2.65	33.31	$a_0 = 38.5$ $c_0 = 3.6$
	(110)	3.82	23.11	
	(200)	5.01	17.62	
	(210)	6.91	12.78	
	(300)	7.38	11.97	
	(220)	9.13	9.68	
	(001)	24.92	3.57	
3 Col_h	(100)	3.95	22.35	$a_0 = 25.8$ $c_0 = 3.5$
	(110)	6.66	13.26	
	(200)	7.74	11.41	
	(001)	25.53	3.49	

[a] Col_h and Col_r denote hexagonal and rectangular columnar phases, respectively

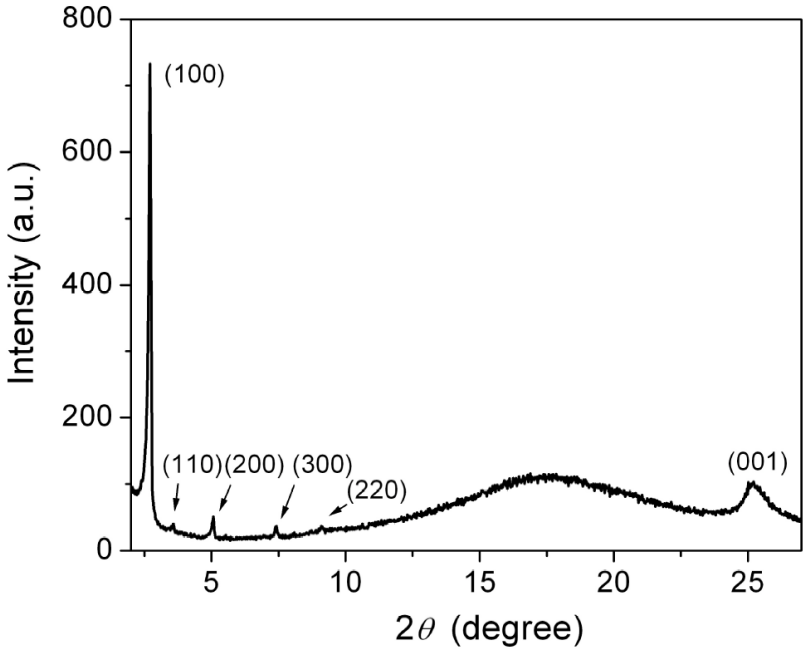

Figure S9. X-ray diffractogram for a film of **2b** at 100 °C.