

## Supplementary materials

X-Ray diffraction studies were carried out on a Rigaku RAXIS rapid diffractometer using Cu K $\alpha$  radiation, a graphite monochromator and a Fujifilm Co., Ltd curved image plate (460 mm x 256 mm). A 0.1 mm collimator was used and typical irradiation times were of 30 minutes. Samples were heated to isotropic to load in capillaries. The nitrogen heater was supplied by Rigaku along with the diffractometer.

**Table 1** Comparison of X-ray diffraction data for compounds 1a-b, 2a-b and 3 obtained with the previous N<sub>2</sub> heating system and with the capillary furnace (Col<sub>ho</sub>: ordered hexagonal columnar; Col<sub>ro</sub>: ordered rectangular columnar).

Compound	Temperature (°C)	N <sub>2</sub> Heating System			Capillary Furnace		
		d-spacing (Å)	Miller Indices ( <i>hkl</i> )	Phase (lattice constant) <sup>a</sup>	d-spacing (Å)	Miller Indices ( <i>hkl</i> )	Phase (lattice constant) <sup>a</sup>
1a	160	16.2	(100)	Col <sub>ho</sub>	16.8	(100)	Col <sub>ho</sub>
		4.1	alkyl halo	(18.7 Å)	4.2	alkyl halo	(19.4 Å)
1b	125	3.5	$\pi$ - $\pi$		3.5	$\pi$ - $\pi$	
		19.3	(100)	Col <sub>ho</sub>	20.0	(100)	Col <sub>ho</sub>
		-	(110)	(22.3 Å)	11.6	(110)	(23.1 Å)
2a	200	4.4	alkyl halo		4.2	alkyl halo	
		3.5	$\pi$ - $\pi$		3.5	$\pi$ - $\pi$	
		16.6	(100)	Col <sub>ho</sub>	16.9	(100)	Col <sub>ho</sub>
		-	(110)	(19.2 Å)	9.8	(110)	(19.5 Å)
2b	135	4.3	alkyl halo		4.3	alkyl halo	
		3.6	$\pi$ - $\pi$		3.6	$\pi$ - $\pi$	
		22.8	(200)	Col <sub>ro</sub>	23.6	(200)	Col <sub>ro</sub>
3	165 (heating)	17.5	(110)	(45.6 Å, 18.9 Å)	18.1	(110)	(47.2 Å, 19.6 Å)
		11.6	(400)		11.9	(400)	
		9.6	(020)		9.7	(020)	
		8.9	(220)		9.1	(220)	
		-	(420)		7.9	(420)	
		4.3	alkyl halo		4.4	alkyl halo	
		3.5	$\pi$ - $\pi$		3.5	$\pi$ - $\pi$	
3	145 (cooling)	Unable to obtain a diffraction pattern			5.2	(100)	Col <sub>ho</sub>
					20.0	alkyl halo	(Å)
					24.1	$\pi$ - $\pi$	
					5.2	(100)	Col <sub>ho</sub>
3	145 (cooling)				9.0	(110)	(Å)
					20.5	alkyl halo	
					24.9	$\pi$ - $\pi$	

<sup>a</sup> Estimated standard uncertainties:  $\pm 0.5$  Å. Additional variations in the temperature dependant lattice constants are expected due to the large uncertainty in temperature associated with the nitrogen heater (estimated uncertainty of  $\pm 5^\circ\text{C}$ ).

## References

- Foster, E. J., Lavigueur, C., Ke, Y.-C. & Williams, V. E. (2005). *J. Mater. Chem.* **15**, 4062-4068.  
 Foster, E. J., Jones, R. B., Lavigueur, C. & Williams, V. E. (2006). *J. Am. Chem. Soc.* **128**, 8569-8574.