Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

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for

Switching from columnar to calamitic mesophases in a new class of rod-like thienoviologens

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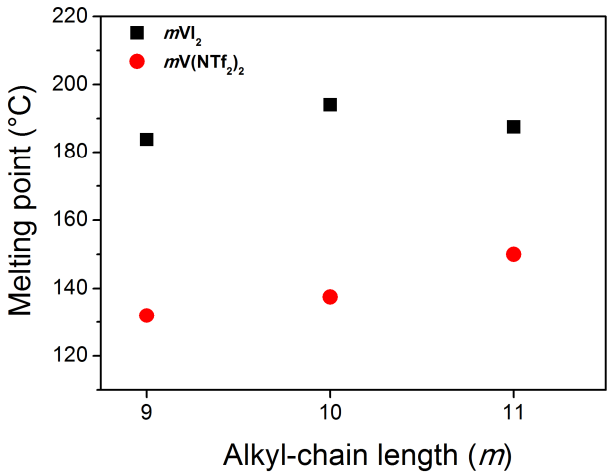

Fig. S1 Melting point *vs*. alkyl-chain length (*m*) for compounds ***m*V(I)$_2$** and ***m*V(NTf$_2$)$_2$** with *m* = 9-11.

PXRD data for *m*V(NTf$_2$)$_2$.

Table S1

Compound	Mesophase lattice constants/Å	d_{meas}/ Å (d_{calcd}/ Å)	Miller indice] *hk*
9V(NTf$_2$)$_2$	Col$_r$ at 120°C (on cooling) *a* = 55.8 Å *b* = 22.6 Å	27.91 (27.91) 20.94 (20.94) 14.42(14.36) 13.76 (13.95) 8.76 (8.77) 6.99 (6.98) 6.49 (6.63) 5.27 (5.24)	20 11 31 40 42 33 43 44
	Col$_r$ at 90°C (on cooling) *a* = 54.2 Å *b* = 22.0 Å	27.11 (27.11) 20.36 (20.36) 13.68(13.96) 8.46 (8.53) 7.01 (7.07) 5.96 (6.07) 5.24 (5.26)	20 11 31 42 23 53 34

Table S2

Compounds	Mesophase lattice constants/Å	d_{meas}/ Å (d_{calcd}/ Å)	Miller indice] *hk*
10V(NTf$_2$)$_2$	Col$_L$ at 90°C (oncooling) *a* = 4.7 Å *b* = 20.3 Å *c* = 30.3 Å	30.33 (30.33) 20.33 (20.33) 14.95(15.20) 7.56 (7.58) 5.07 (5.08) 4.68 (4.68) 4.57 (4.56)	001 01 002 004 04 10 11
11V(NTf$_2$)$_2$	Col$_r$ at 130°C (on heating) *a* = 51.4 Å *b* = 41.3 Å	32.20 (27.11) 25.72 (25.72) 19.26(19.16) 16.06 (16.10) 8.51 (8.84) 7.50 (7.44) 6.55 (6.44)	11 20 12 22 34 35 55

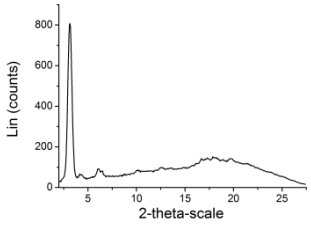

Fig. S2 Powder pattern of **9V(NTf$_2$)$_2$** recorded at 120 °C on heating.

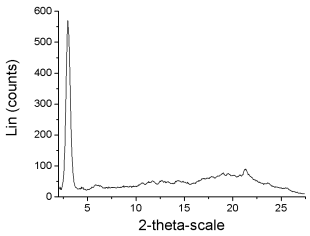

Fig. S3 Powder pattern of **10V(NTf$_2$)$_2$** recorded at room temperature on cooling from the isotropic liquid state.

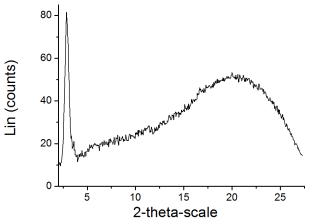

Fig. S4 Powder pattern of **11V(NTf$_2$)$_2$** recorded at room temperature after cooling from the isotropic liquid state under planar alignment conditions.

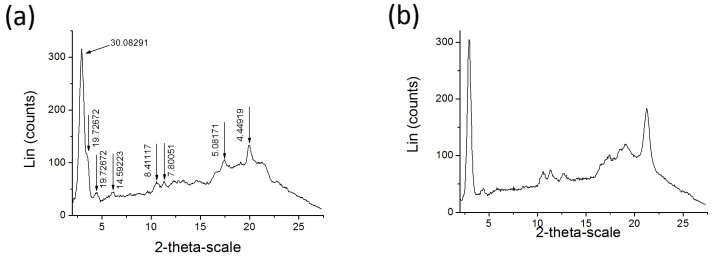

Fig. S5 Powder pattern of **11V(NTf$_2$)$_2$** recorded at room temperature after the first (a) and second (b) cooling scan from the isotropic liquid state.

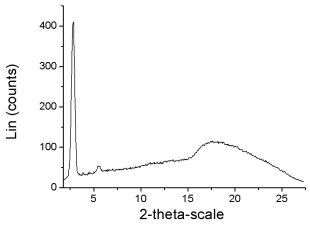

Fig. S6 Powder pattern of **11V(NTf$_2$)$_2$** recorded at 130 °C in the 2nd heating scan.