

Supplementary Information

Supramolecular Architecture Elucidation of the Room Temperature Columnar Mesophases

Exhibited by Mixed-Valent Diruthenium Alkoxybenzoates

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Some specific synthetic procedures

Ru₂(3,4,5-B3OC2)₄Cl was synthesized from Ru₂(O₂(CH₂)₂CH₃)₄Cl²⁶ by a methatesis reaction. Both Ru₂(O₂(CH₂)₂CH₃)₄Cl (124 mg, 0.21 mmoles) and 3,4,5-tri(ethoxy)benzoic acid (300 mg, 1.18 mmoles) were dissolved in 20 mL EtOH and refluxed for 3 hours (total precipitation). The red-brown precipitate was filtered and redissolved in CHCl₃. After doing so, ethanol was added in order to reprecipitate the complex and the solution was heated to evaporate the CHCl₃. After complete precipitation of the red-brown complex, the solid was filtrated. This dissolution/reprecipitation cycle was repeated until no free 3,4,5-triethoxybenzoic acid was detected by IR (Total yield: 95%). IR data (KBr nulls, Avatar 320 spectrometer): 2979 (m, n(CH₃,as)), 2932 (m, n(CH₂,as)), 2886 (w, n(CH₃,s)), 1587 (m, n(CO₂,as)), 1359 (s,n(CO₂,s)), 1411 (s, n(C=C) aromatic ring deformations), 1456 and 1381 cm⁻¹ (s, d(CH₂,as), d(CH₃,as)), d(CH₃,s)).

The solvent for crystallization was chosen after systematic solubility studies: Ru₂(3,4,5-B3OC2)₄Cl was found to be soluble at room temperature in CHCl₃, acetone and toluene, as well as in hot methanol and ethanol. It was slightly soluble in diethyl ether, and insoluble in water. The compound was then dissolved in refluxing methanol and the solution was allowed to cool slowly until it reached room temperature (approx. 8 hours). After 3 days, needle red crystals suitable for structural analysis were collected.

Ru₂(3,4,5-B3OC6)₄Cl: 49.6 mg Ru₂(but)₄Cl were added to 50 mL EtOH containing 350 mg 3,4,5-tri(hexyloxy)benzoic acid. After three days, the solution was evaporated to dryness, the solid mixture

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was dissolved in CH₃Cl then the same volume of MeOH was added; after CH₃Cl evaporation, a waxy red-brown precipitate was filtered and dried under vacuum overnight.

Ru₂(3,4,5-B3OC8)₄Cl: 50 mg Ru₂(but)₄Cl were added to 50 mL EtOH containing 350 mg 3,4,5-tri(octyloxy)benzoic acid. A waxy red-brown precipitate appeared after a few hours; it was filtered and dried under vacuum overnight.

Table S1 – Elemental analysis and yields for the synthesis of Ru₂(x,y,z-BmOCn)₄Cl compounds.

Compound	n	% C exp. (calc.)	% H exp. (calc.)	Yield (%)
Ru ₂ (3,4,5-B3OCn) ₄ Cl	2	50.39 (49.93)	5.48 (5.80)	95
	6	62.00 (62.43)	8.52 (8.59)	n.d.
	8	65.88 (65.87)	9.61 (9.45)	41
	10	67.32 (68.44)	10.02 (10.09)	56
	12	69.32 (70.41)	10.57 (10.58)	n.d.
	14	71.50 (71.97)	11.26 (10.97)	62
	16	72.85 (73.25)	11.50 (11.29)	n.d.
	18	73.80 (74.31)	11.55 (11.55)	57
Ru ₂ (3,4-B2OCn) ₄ Cl	10	66.58 (65.77)	9.70 (9.20)	61
	14	68.90 (69.45)	9.91 (10.16)	63
	18	71.60 (71.98)	11.18 (10.82)	72
Ru ₂ (3,5-B2OCn) ₄ Cl	8	63.17 (63.22)	8.71 (8.53)	47
	10	65.60 (65.77)	9.27 (9.19)	63
	14	69.38 (69.45)	10.20 (10.16)	82
	18	71.46 (71.98)	10.89 (10.82)	74

Solubility:

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All $\text{Ru}_2(3,4\text{-B}2\text{OCn})_4\text{Cl}$ derivatives synthesized are insoluble both in cold methanol or ethanol, but soluble in cold CHCl_3 and hot *n*-heptane. Synthesized compounds belonging to the $\text{Ru}_2(3,5\text{-B}2\text{OCn})_4\text{Cl}$ and $\text{Ru}_2(3,4,5\text{-B}3\text{OCn})_4\text{Cl}$ series are also insoluble in cold methanol or ethanol; they all dissolve in cold CHCl_3 and in *n*-heptane, except for the lighter homologues $\text{Ru}_2(3,4,5\text{-B}3\text{OC1})_4\text{Cl}$ and $\text{Ru}_2(3,4,5\text{-B}3\text{OC2})_4\text{Cl}$, which are only partly soluble in cold CHCl_3 and in hot *n*-heptane.

Table S2 - Main IR bands for $\text{Ru}_2(x,y,z\text{-BmOCn})_4\text{Cl}$ compounds (References: vs: very strong, s: strong; m: medium; w: weak; v: stretching; δ : bending; s: symmetric; as: assymmetric. assignments based on references. 11, S47 and S48).

Wavenumber (cm^{-1}) (Intensity)			Proposed assignment
3,4,5-B3OCn	3,4-B2OCn	3,5-B2OCn	
2955(w), 2920(vs), 2855(m)			v(CH_3 ,as), v(CH_2 ,as), v(CH_2 ,s)
1455(s), 1414(m) ^a	1456(s), 1384(s) ^b	1466(s), 1410(s)	v(CO_2 ,as), v(CO_2 ,s)
1588(s)	1597(m), 1520(d,w)	1597 (m)	v($\text{C}=\text{C}$) (aromatic ring deformations)
1466(m), 1390(s) 1420-1425(w)			($\delta(\text{CH}_2$,as), δ(CH_3 ,as)), ($\delta(\text{CH}_3$,s)) δ(CH_2 ,as) (α to ether group)
1229(m), 1113(m)	1425(s), 1273(s), 1230(m), 1124(m)	1169(m), 1057(m)	Others bands
721(w)			δ(CH_2) _n (rocking)

^a detected at 1683 (s) and 1322 (m) cm^{-1} for the free carboxylic acids.^b detected at 1669, 1679 (w, s) and 1278 (m) cm^{-1} for the free carboxylic acids.^c detected at 1694 (s) and 1303 (m) cm^{-1} for the free carboxylic acids.

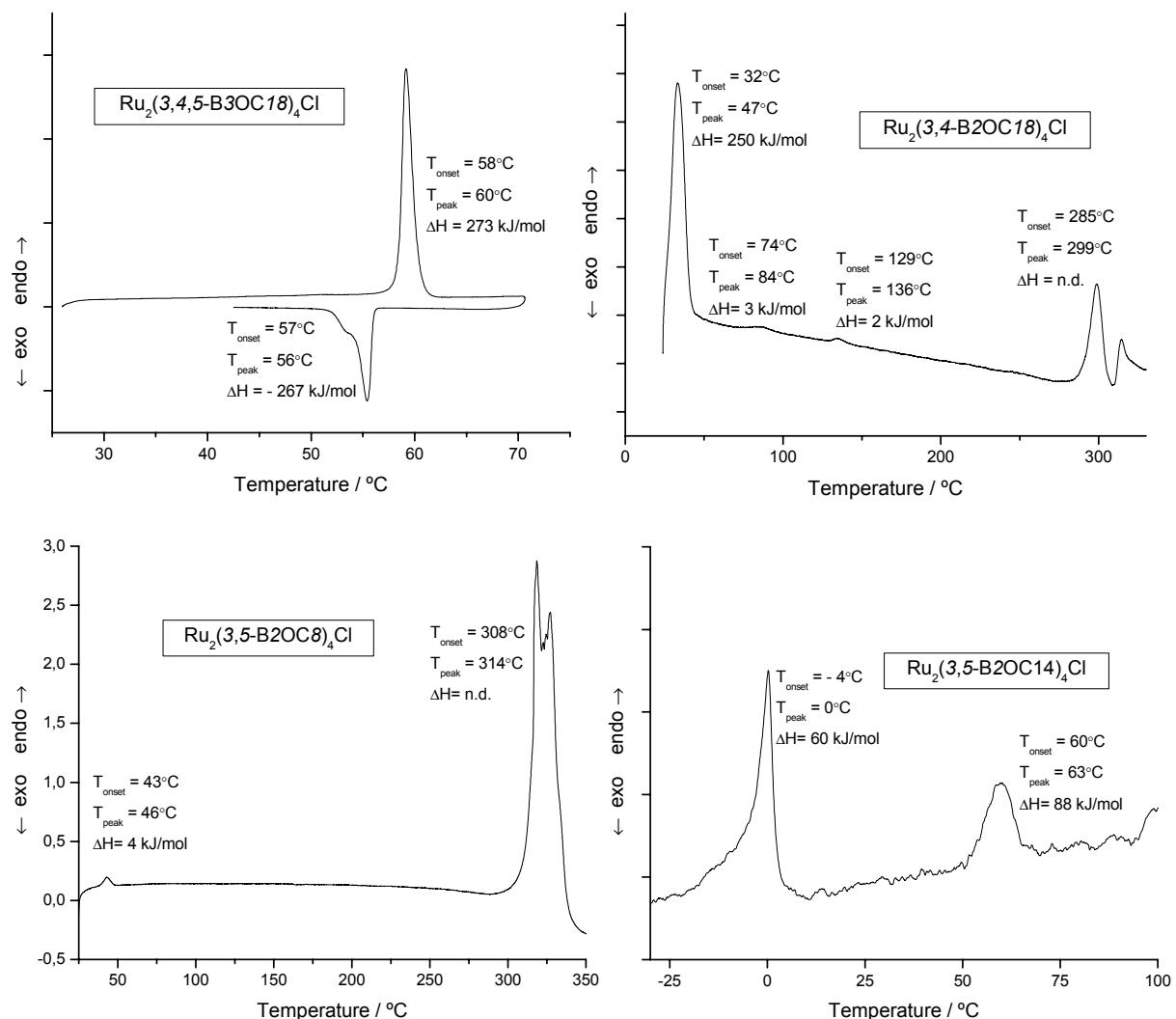
**Figure S1** – Some representative DSC traces of the studied compounds.

Table S3 – Structural data, as determined from XRD experiments, for selected compounds at given temperatures. d (interplane distance) and D (intercolumnar or interlamellar distance) in Å, temperatures in °C. vs: very strong, s: strong, m: medium intensity, w: weak, vw: very weak, b: broad, dif: diffuse.

Ru₂(3,5-B₂OC₁₈)₄Cl

d _{exp}	Intensity	Index (hk)	d _{calc}	Phase	D/Temp
26.38	vs	10	26.38	Col _H	30.47
15.21	s	11	15.23	p6mm	100
13.14	m	20	13.19		--

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9.99	w	21	9.97		--
8.82	vw	30	8.79		--
7.37	vw	31	7.32		--
6.1	vw, b	Stack	--		--
4.8	m,b	Alkyl Chains	--		--

Ru₂(3,5-B2OC14)₄Cl

<i>d</i>_{exp}	Int	Index (hk)	<i>d</i>_{calc}	Phase	D/Temp
23.58	vs	10	23.58	Col _H	27.23
13.59	m	11	13.61	<i>p</i> 6mm	120
11.86	w	20	11.79		--
8.93	vw	21	8.91		--
7.91	vw	30	7.86		--
6.81	vw	22	6.81		--
6.57	vw	31	6.54		--
4.76	vw, b	Alkyl chains	--		--

Ru₂(3,5-B2OC10)₄Cl

<i>d</i>_{exp}	Int	Index (hk)	<i>d</i>_{calc}	Phase	D/Temp
20.63	vs	10	20.63	Col _H	23.82
11.92	m	11	11.91	<i>p</i> 6mm	100
10.32	m	20	10.31		
7.82	w	21	7.81		
6.93	vw	30	6.88		
5.97	vw	22	5.95		
5.75	vw	31	5.72		

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4.76	w, dif	Alkyl chains	--		
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Ru₂(3,5-B2OC8)₄Cl

d_{exp}	Int	Index (hk)	d_{calc}	Phase	D/Temp
18.93	vs	10	18.93	Col _H	21.86
10.93	m	11	10.93	p6mm	100
9.48	w	20	9.47		
7.17	w	21	7.16		
6.3	vw	30	6.31		
4.9	w, dif	alk.chains	--		

Ru₂(3,4-B2OC18)₄Cl

d_{exp}	Int	Index (hk)	d_{calc}	Phase	D/Temp
28.25	vs	10	28.25	Col _H	32.62
16.45	m	11	16.31	p6mm	130
14.27	m	20	14.12		
10.78	w	21	10.68		
5.6	vw, dif	Stack	--		
4.7	w, dif	Alkyl chains	--		

Ru₂(3,4-B2OC14)₄Cl – Lamellar phase

d_{exp}	Int	Index (00l)	d_{calc}	Phase	D/Temp
29.87	s	001	29.87	Lamellar	29.87
14.48	m	002	14.93		80
10.25	vw	003	9.96		

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7.54	vw	004	7.47		
5.88	vw	005	5.97		
5.5	vw	Stack	--		
4.6	w, dif	Alkyl chains	--		

Ru₂(3,4-B2OC14)₄Cl – Columnar phase

d_{exp}	Int	Index (hk)	d_{calc}	Phase	D/Temp
25.21	vs	10	25.21	Col _H	29.11
14.51	m	11	14.55	p6mm	140
12.61	w	20	12.63		
9.71	vw	21	9.53		
5.6	vw	Stack	--		
4.9	w, dif	Alkyl chains	--		

Ru₂(3,4-B2OC10)₄Cl – Lamellar phase

d_{exp}	Int	Index (00l)	d_{calc}	Phase	D/Temp
25.44	s	001	25.44	Lamellar	25.44
12.82	w	002	12.72		100
5.7	vw	Stack	--		
4.7	w; dif	Alkyl chains	--		

Ru₂(3,4-B2OC10)₄Cl – Columnar phase

d_{exp}	Int	Index (hk)	d_{calc}	Phase	D/Temp
23.03	vs	10	23.03	Col _H	26.59
13.14	m	11	13.30	p6mm	180

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11.39	w	20	11.52		
8.71	vw	21	8.70		
5.7	vw	stack	--		
4.8	w; dif	alkyl chains	--		

Ru₂(3,4,5-B₃OC₁₀)₄Cl

d_{exp}	Intensity	Index (hk)	d_{calc}	Phase	D/Temp
23.34	vs	10	23.69	Col _H	26.95
13.68	s	11	13.69	p6mm	60
11.82	s	20	11.852		--
8.95	s	21	8.96		--
7.90	m	30	7.90		--
6.85	w	22	6.84		
6.58	w	31	6.57		--
5.94	vw	40	5.92		
6.2	vw	Stack	--		--
4.7	w	Chains	--		--

Ru₂(3,4,5-B₃OC₁₈)₄Cl

d_{exp}	Intensity	Index (hk)	d_{calc}	Phase	D/Temp
30.99	vs	10	30.95	Col _H	30.95
18.11	m	11	17.89	p6mm	80
15.72	m	20	15.50		--
11.82	w	21	11.71		--
6.1	vw	Stack	--		--
4.7	w	Chains	--		--

Supplementary Material (ESI) for Journal of Materials Chemistry

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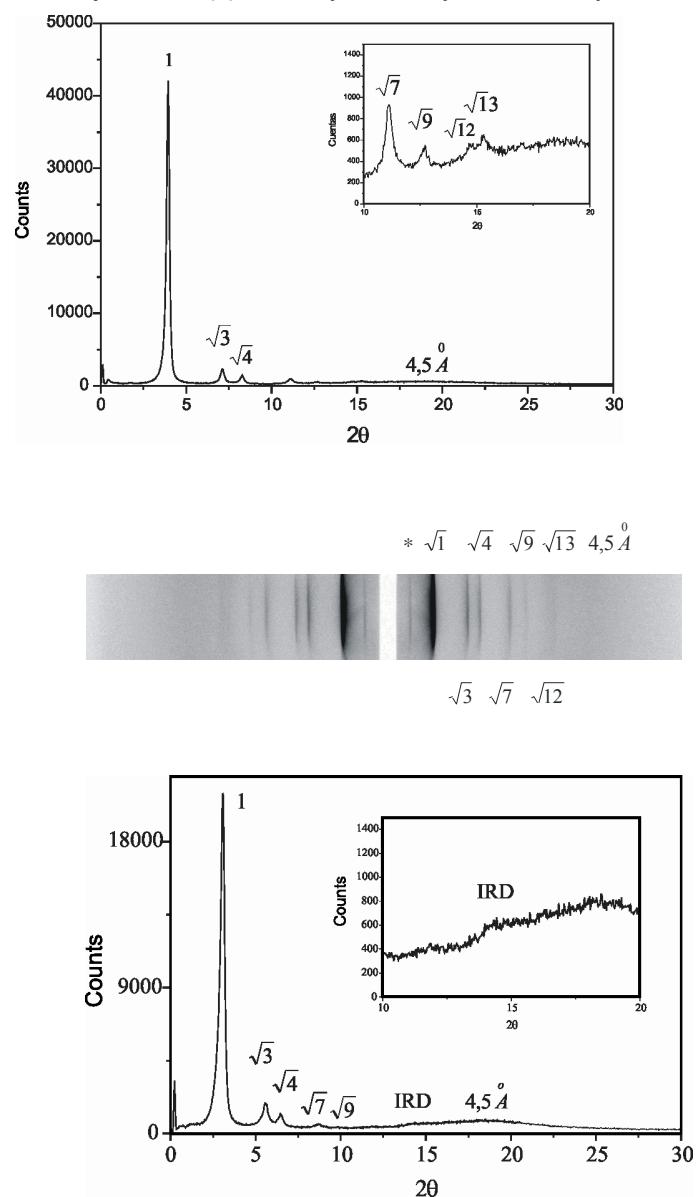


Figure S2 - XRD patterns corresponding to the Col_h mesophases of (a) Ru₂(3,5-B₂OC₁₀)₄Cl at 60 °C, (b) same compound at 100 °C, (c) Ru₂(3,5-B₂OC₁₈)₄Cl, as detected at 100 °C

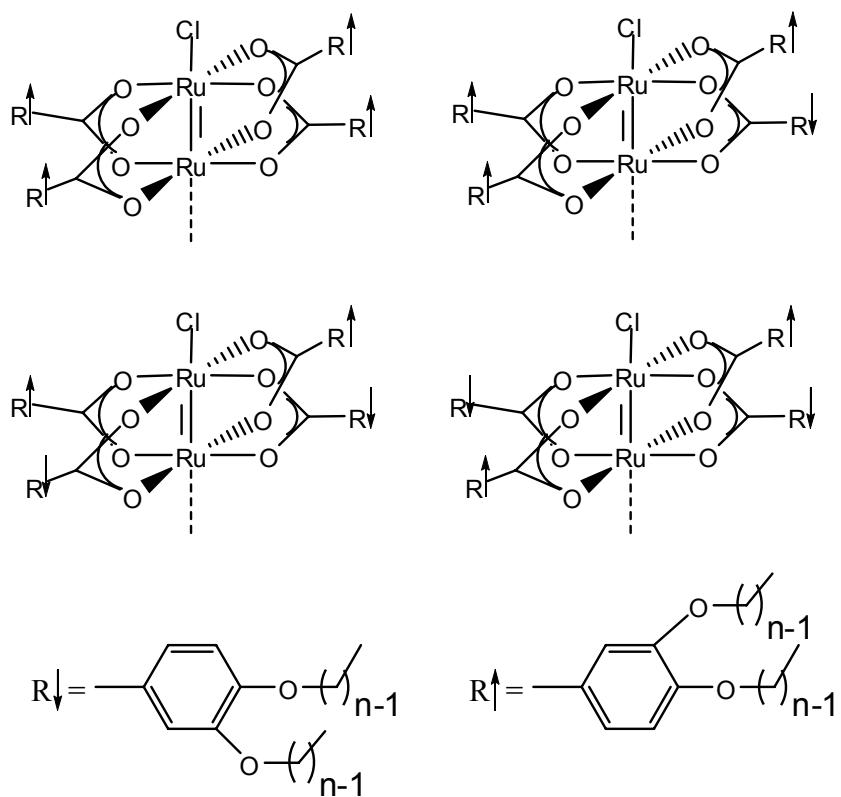


Chart S1 – Possible conformers for $\text{Ru}_2(3,4\text{-B}_2\text{OC}_n)_4\text{Cl}$

Magnetic susceptibility measurements results

Experimental molar magnetic susceptibility data were corrected from diamagnetism as explained in the experimental section. The corrected data from 12 to 250 K were fitted with the usual equations, which describe a collection of $S = 3/2$ spin centers undergoing a strong Zero Field Splitting and weak antiferromagnetic interactions, which were treated within the frame of the mean molecular field approximation. Values below 12 K were discarded because of the presence of small amounts of paramagnetic interactions (which contributes largely to the measured susceptibility at very low temperatures) and the limitations of the approximations related to the Van Vleck equation; values above the slope change related to the phase transition have also been discarded. As usual, a term describing the presence of a small proportion (ρ) of a $S = 1/2$ paramagnetic impurity was added. The equation used for the refining of magnetic data was then:

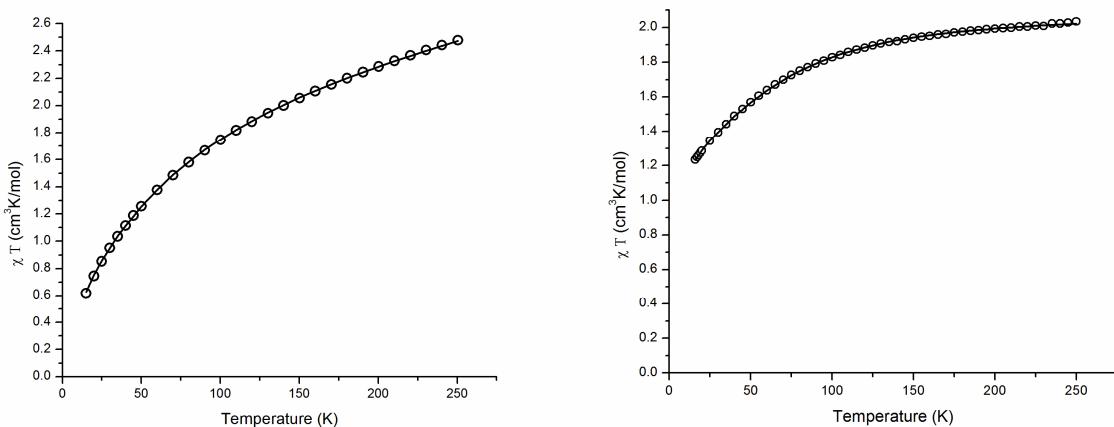
$$\chi_{\text{calc}} = (1 - \rho) \cdot \chi' + \rho \frac{Ng_i^2 \beta^2}{3kT} S_i(S_i + 1), \text{ where}$$

$$\chi' = \frac{\chi_{\text{mol}}}{1 - (2zJ/Ng^2 \beta^2) \chi_{\text{mol}}}, \quad \chi_{\text{mol}} = \frac{1}{3}(\chi_{\parallel} + 2\chi_{\perp}) + \text{TIP}$$

$$\chi_{\parallel} = \frac{Ng_{\parallel}^2 \beta^2}{kT} \cdot \frac{1 + 9e^{-2D/kT}}{4(1 + e^{-2D/kT})} \quad \text{and} \quad \chi_{\perp} = \frac{Ng_{\perp}^2 \beta^2}{kT} \cdot \frac{4 + (3kT/D)(1 - e^{-2D/kT})}{4(1 + e^{-2D/kT})}$$

Fits have been performed on $\chi T(T)$, minimizing $\sigma^2 = \sum (\chi_{\text{calc}} T - \chi_{\text{exp}} T)^2 / \sum \chi_{\text{exp}}^2$ a parameter taken as an estimator of the goodness of fit.

Figure S3 shows the agreement between calculated and experimental values for $\text{Ru}_2(3,4,5-\text{B}_3\text{OC}_{14})_4\text{Cl}$ (a) and $\text{Ru}_2(3,5-\text{B}_2\text{OC}_{18})_4\text{Cl}$ (b), final parameters are collected in table S4.



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Figure S3: Magnetic data and fits for $\text{Ru}_2(3,4,5\text{-B}_3\text{OC}14)_4\text{Cl}$ (a) and $\text{Ru}_2(3,5\text{-B}_2\text{OC}18)_4\text{Cl}$ (b)**Table S4:** Magnetic parameters obtained for the three studied compounds form the fitting procedure described above.

	$\text{Ru}_2(3,4,5\text{-B}_3\text{OC}14)_4\text{Cl}$	$\text{Ru}_2(3,4,5\text{-B}_3\text{OC}10)_4\text{Cl}$	$\text{Ru}_2(3,5\text{-B}_2\text{OC}18)_4\text{Cl}$
D (cm⁻¹)	76	77	80
zJ (cm⁻¹)	- 2.9	- 2.3	- 0.3
g//	2.01	2.01	2.01
g_⊥	2.26	2.27	2.16
TIP	$2.7 \cdot 10^{-3}$	$8 \cdot 10^{-4}$	10^{-5}
g_{imp}	2.00	2.00	2.00
P	0.011	0.0002	0.011
σ GOF	$5.0 \cdot 10^{-6}$	$7.4 \cdot 10^{-6}$	$3.2 \cdot 10^{-6}$

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Table S5 – Temperature dependence of the main Raman bands observed for Ru₂(3,4,5-B₃OC₁₈)₄Cl.

Vibration	Wavenumber (in cm ⁻¹)					
	at 20°C	at 45°C	at 55°C	at 65°C	at 90°C	at 120°C
vRuRu	341	337	336	337	336	336
2vRuRu	673	665	663	663	662	658
3vRuRu	1004	995	996	993	992	990
4vRuRu	1310			1308	1314	n.d.
δ(CH₂,s)	1374			1374	1373	1375
v(CO₂,s)	1410			1409	1409	1410
δ(^aCH₂,as)	1435			1431	1432	1431
v(C=C) (aromatic ring deformations)	1586			1586	1586	1587

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Table S6 – EXAFS studies: final parameters arising from de fits of $\chi \cdot k^n$ vs. k for the first and second shells of the pseudo-radial distribution for compound Ru₂(3,4,5-B3OC10)4Cl both at 25 and 100°C (N = number of atoms of the specified type present in the analyzed shell, R = mean distance for these atoms from the Ru atom, $\Delta\sigma$ = Thermal and static disorder, ΔE = Shift in energy edge, q.o.f.: χ^2 standard deviation of the refinement).

Parameter	25°C – 1 st shell (O atoms)	25°C – 2 nd shell (Ru atoms)	100°C – 1 st shell (O atoms)	100°C – 2 nd shell (Ru atoms)
N	4.08	0.93	4.04	0.84
R	1.99	2.30	1.99	2.29
$\Delta\sigma$	- 9.8*10 ⁻⁶	1.1*10 ⁻⁴	1.4*10 ⁻⁴	1.2*10 ⁻⁶
ΔE	-0.019	-0.79	-0.679	-2.6
g.o.f.	1.4*10 ⁻⁵	1.0*10 ⁻⁵	5*10 ⁻⁶	6.1*10 ⁻⁶

Calculation of the molecular volumes

As explained in the text, the “experimental” molecular volumes in the mesophase were calculated from XRD data as $V_o = S * h$. The estimated molecular volumes, V_e , were calculated under the hypothesis of additivity of molecular volumes of the different molecular fragments, as follows:

$$V_e = VRu_2(\text{benzoate})_4\text{Cl} + 4m\text{VOCH}_3 + 4m(n-1)\text{VCH}_2 \quad \text{where,}$$

$$VRu_2(\text{benzoate})_4\text{Cl}^{S49} = 698.69\text{\AA}^3$$

$$\text{VOCH}_3 = \frac{1}{4}(VRu_2(4-\text{B1OC1})_4\text{Cl} * 0.25\text{H}_2\text{O} - VRu_2(\text{benzoate})_4\text{Cl} - 0.25\text{VH}_2\text{O}) = 38.9\text{\AA}^3.$$

$$VRu_2(4-\text{B1OC1})_4\text{Cl} * 0.25\text{H}_2\text{O}^{46} = 3447\text{\AA}^3 \quad (Z=4), \quad VH_2\text{O} = 29.9\text{\AA}^3.$$

and VCH_2 values have been calculated as $\text{VCH}_2(T) = 26.5616 + 0.02023 * T$ ($\text{\AA}^3/\text{methylene}$) at the corresponding temperature in each case (the temperature dependence of the volume of the rigid core has been neglected). V_e estimated values are compared to V_o values in table S6. Dilatometry results validating the calculated V_e values (see text) are shown on Figure S4.

Table S7 – Molecular volumes from XRD data (V_o , calculated as $V_o = S^*h$, uncertainty in the last digits between parenthesis) compared to the molecular volumes estimated as a sum of the different molecular parts (V_e), as described in the text.

Compound	T (°C)	V_o (Å ³)	V_e (Å ³)
Ru ₂ (3,4,5-B ₃ OC ₆) ₄ Cl	90	2840 (70)	2809
Ru ₂ (3,4,5-B ₃ OC ₈) ₄ Cl	90	3490 (90)	3476
Ru ₂ (3,4,5-B ₃ OC ₁₀) ₄ Cl	90	4000 (100)	4143
Ru ₂ (3,4,5-B ₃ OC ₁₂) ₄ Cl	90	4600 (110)	4810
Ru ₂ (3,4,5-B ₃ OC ₁₄) ₄ Cl	90	5410 (130)	5577
Ru ₂ (3,4,5-B ₃ OC ₁₈) ₄ Cl	90	6730 (150)	6811
Ru ₂ (3,5-B ₂ OC ₈) ₄ Cl	100	2480 (140)	2580
Ru ₂ (3,5-B ₂ OC ₁₀) ₄ Cl	100	2950 (160)	3030
Ru ₂ (3,5-B ₂ OC ₁₄) ₄ Cl	100	3760 (200)	3930
Ru ₂ (3,5-B ₂ OC ₁₈) ₄ Cl	100	4750 (240)	4830
Ru ₂ (3,4-B ₂ OC ₁₀) ₄ Cl	160	3450 (180)	3120
Ru ₂ (3,4-B ₂ OC ₁₄) ₄ Cl	160	4150 (220)	4060
Ru ₂ (3,4-B ₂ OC ₁₈) ₄ Cl	160	5130 (260)	5000

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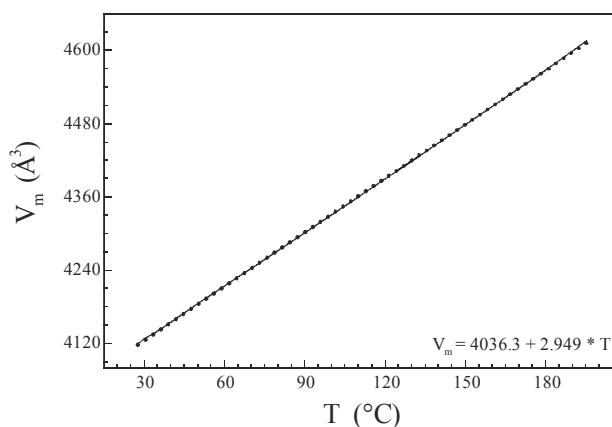
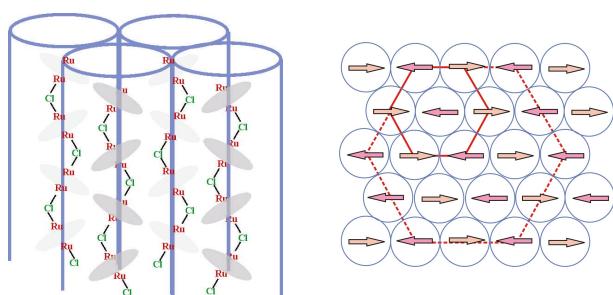


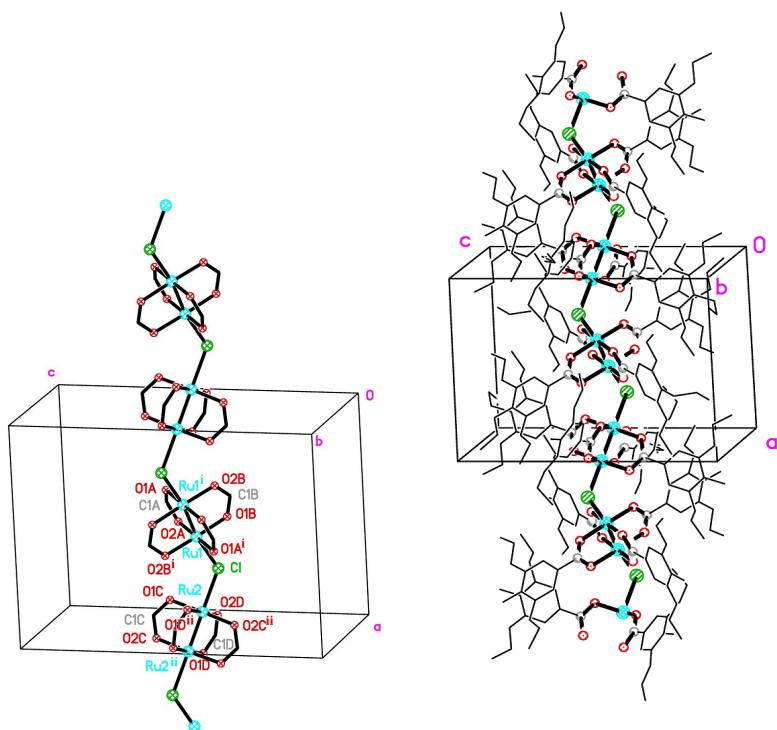
Figure S4: Dilatometry experiments: temperature dependence of the molecular volume for $\text{Ru}_2(3,4,5\text{-B}_3\text{OCl}_{10})_4\text{Cl}$

A possible explanation for the “superstructure”

The Bragg peaks observed at $2 d_{10}$ for some compounds can be understood in the terms of the suggested structural model, taking into account the different orientations the polymeric strands can exhibit. Indeed, the cores of neighbouring strands can be shifted by 180° referred to the tilt with respect to the columnar axis (as depicted in Figure S5). Even if the diffraction element is always the same, its non-strictly equivalent position could give rise to a signal in the XRD pattern, much weaker than that corresponding to d_{10} , at twice this distance. This peak is only visible for the $\text{Ru}_2(3,5\text{-B}_2\text{OCl}_n)_4\text{Cl}$ series, where d_{10} is a very strong signal, and not for the $\text{Ru}_2(3,4\text{-B}_2\text{OCl}_n)_4\text{Cl}$ series, whose diffraction patterns are much less intense.



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Figure S5 – Side and upper views of the suggested model for the superstructure found in the 3,4-derivatives.**Figure S6** – Schematic representation of the polymeric backbone of $\text{Ru}_2(3,4,5\text{-B}_3\text{O}_2)_4\text{Cl}$, showing the labeling scheme, and view of a segment of one *zig-zag* polymeric strand of the same compound.Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$.**Table S8** - Selected geometric parameters (\AA)

Ru1—O1A ⁱ	2.017 (4)	Ru2—O1C	2.018 (4)
Ru1—O1B	2.019 (4)	Ru2—O2D	2.022 (3)
Ru1—O2B ⁱ	2.020 (4)	Ru2—O2C ⁱⁱ	2.025 (4)
Ru1—O2A	2.021 (4)	Ru2—O1D ⁱⁱ	2.028 (4)
Ru1—Ru1 ⁱ	2.2807 (9)	Ru2—Ru2 ⁱⁱ	2.2788 (9)
Ru1—Cl	2.5266 (16)	Ru2—Cl	2.5137 (17)

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Ru1 ⁱ —Ru1—Cl	170.15 (5)	Ru2—Cl—Ru1	116.74 (7)
Ru2 ⁱⁱ —Ru2—Cl	171.79 (5)		

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+2, -y+1, -z+1$.

The raw material, as synthesized, is not solvated. When recrystallized from methanol, however, a depleted water molecule is trapped in the vicinity of the chlorine atoms and a few suspicious cavities (ca. 100 Å³ in volume) appear in the 3D structure which very probably lodges a solvent molecule. The final Difference Fourier does not show any concentrated electron density in these cavities; therefore, the water or methanol solvato molecules therein ought to be highly disordered, if present at all. Unfortunately, a more detailed analysis of the situation via alternative techniques (like TGA, etc) has been so far precluded since the single crystals used for the structural work were extremely rare specimens from a very sparse batch, the result of a fortuitous, up to now irreproducible recrystallization.

Additional references for Supplementary Information

- S47) D. Lin-Vien, N. Colthup, W. Fateley and J. Grasselli, in *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Press, Inc., 1991.
- S48) K. Nakamoto, in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, ed. John Wiley & Sons, 4th edn., 1986.
- S49) M. Abe, Y. Sasaki, T. Yamaguchi and T. Ito, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1585.