



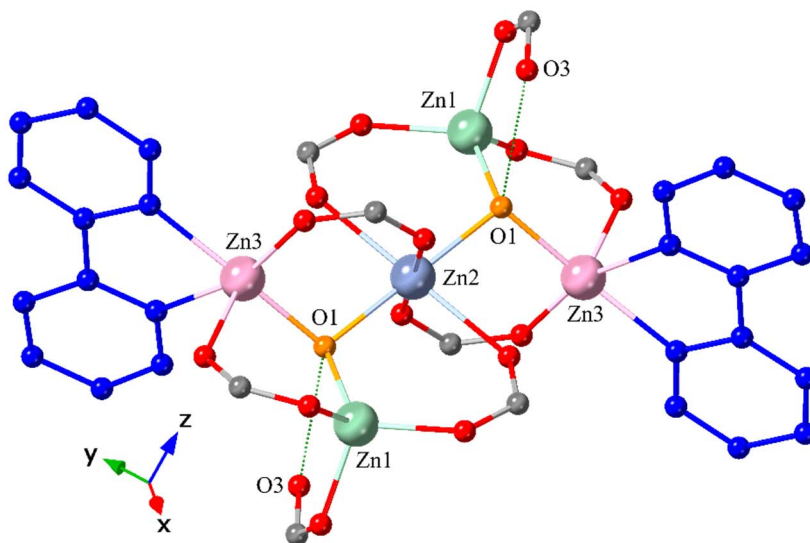
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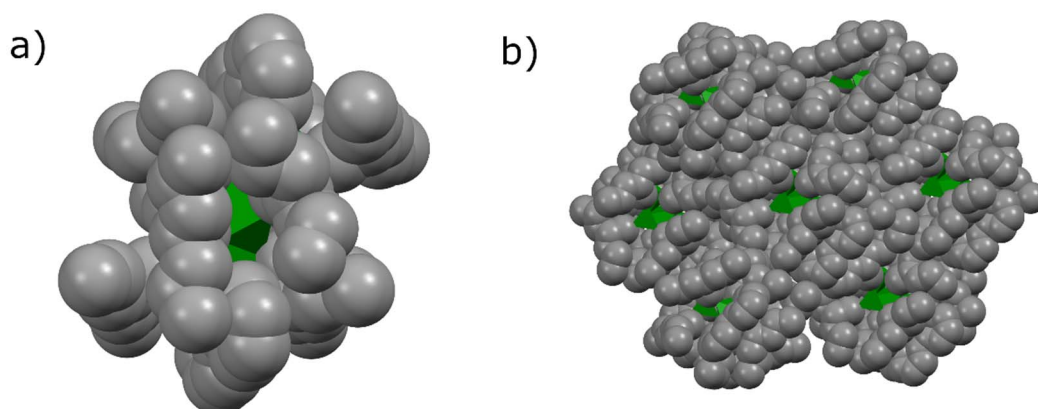
**Supporting information for article:**

**Combining valproate and bipyridyl ligands to construct a 0D core-shell  $Zn_5(\mu_3-OH)_2$  cluster and a 2D layered coordination network with a  $[Zn_3(\mu_3-OH)]_2$  SBU**

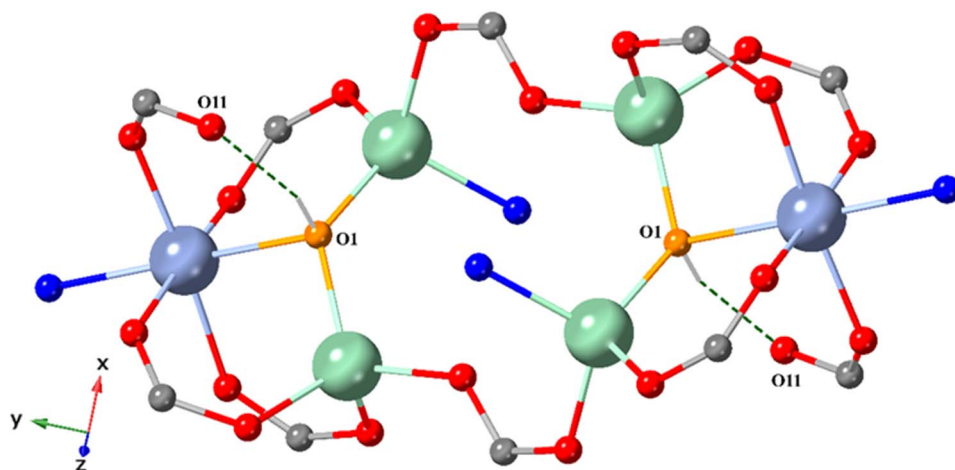
**Hijazi Abu Ali and Mohanad Darawsheh**



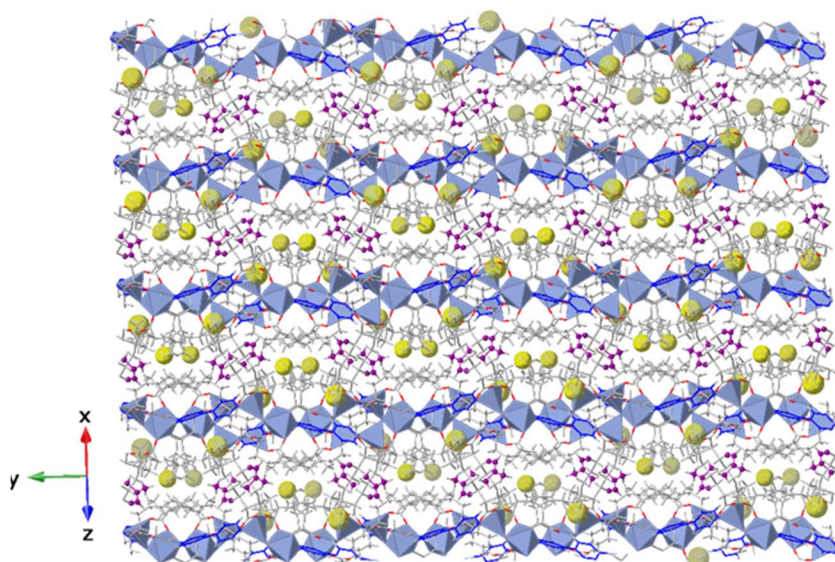
**Figure S1** Intramolecular hydrogen bond in **II** shown as dashed green line.



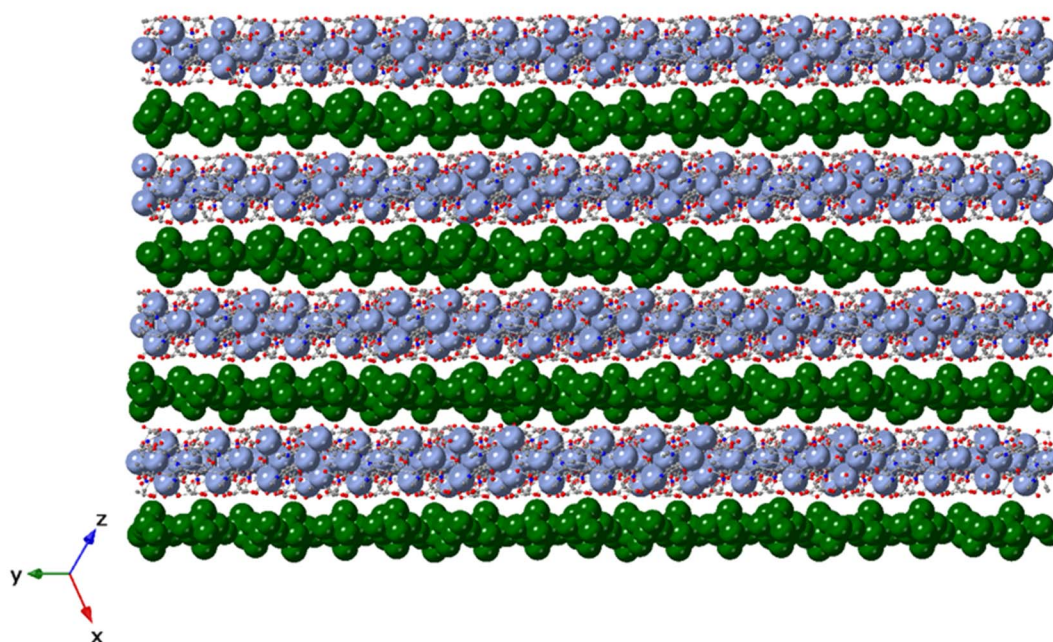
**Figure S2** The encapsulation of Zn<sub>5</sub> clusters in compound **II** inside a carbon shell formed by ligands making well-separated clusters. (a: one molecular unit, b: packing view of adjacent molecules). Grey: C, green polyhedral: Zn<sub>5</sub> clusters.



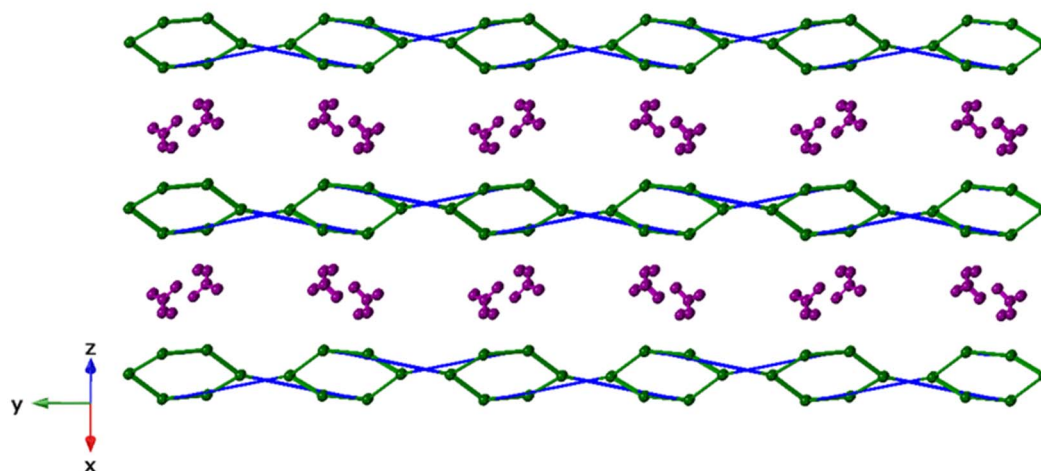
**Figure S3** Intramolecular hydrogen bonding in **III** shown as green dashed lines.



**Figure S4** 2D network layers in **III** separated by valproic-aliphatic chains (grey) and DMF (violet) with internal voids shown in yellow. The voids are well-separated without significant accessible window.

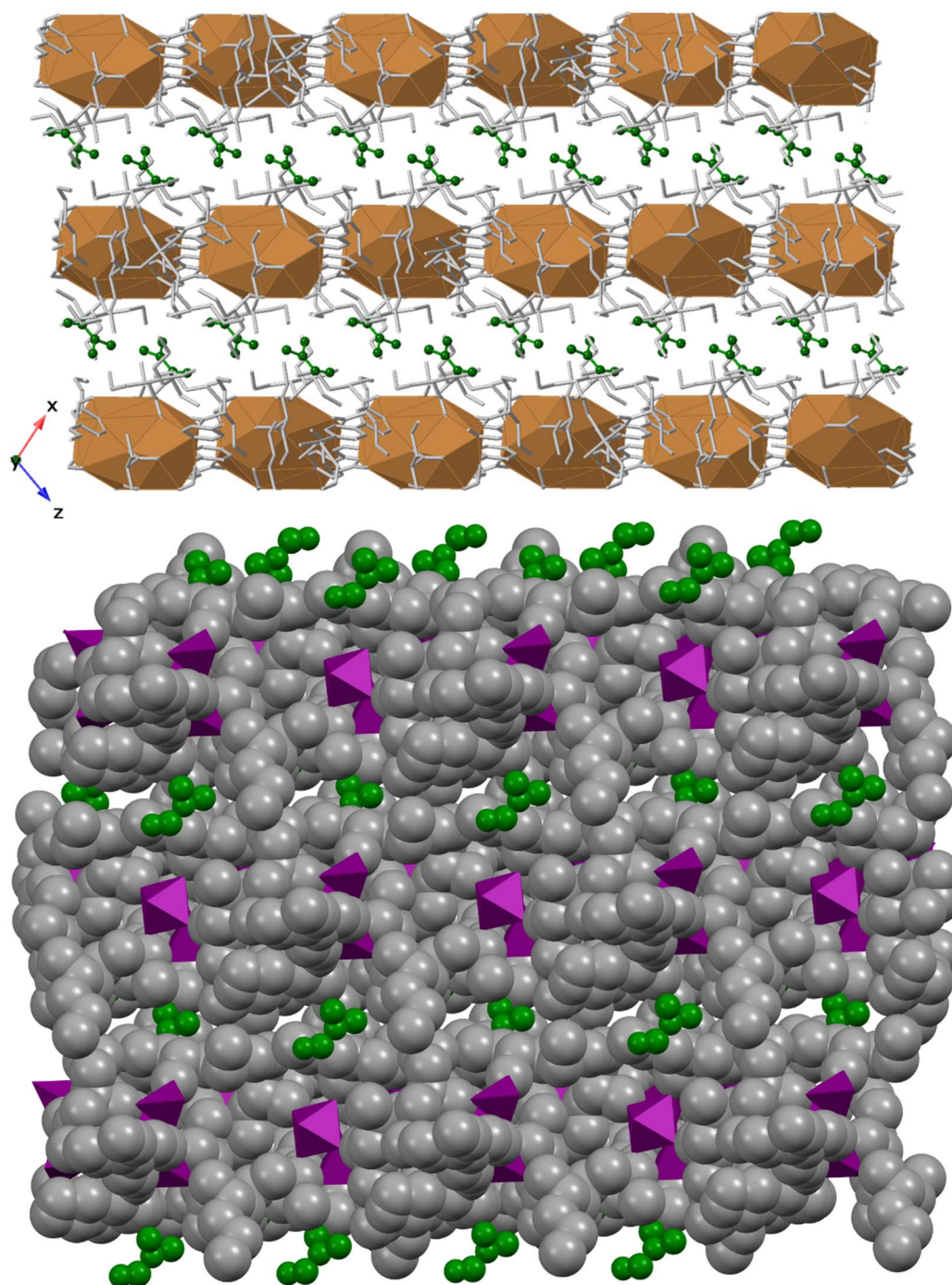


**Figure S5** Alternative layers of 2D network and DMF (green) in **III** are shown in space-fill style. Aliphatic chains were omitted for clarity.

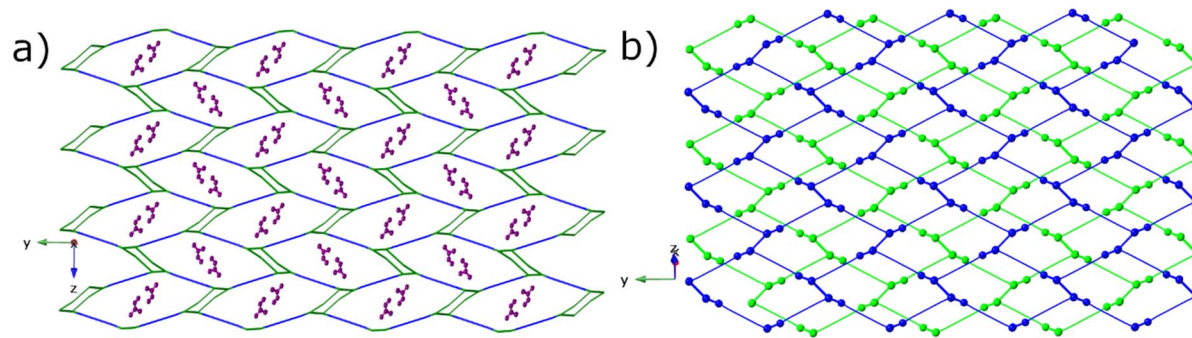


**Figure S6** Simplified view of 2D network and six-membered ring of the SBU of **III** showing the alignment of DMF molecules parallel to the hexagon of the network. Blue lines are the 4,4-bipyridine ligands.

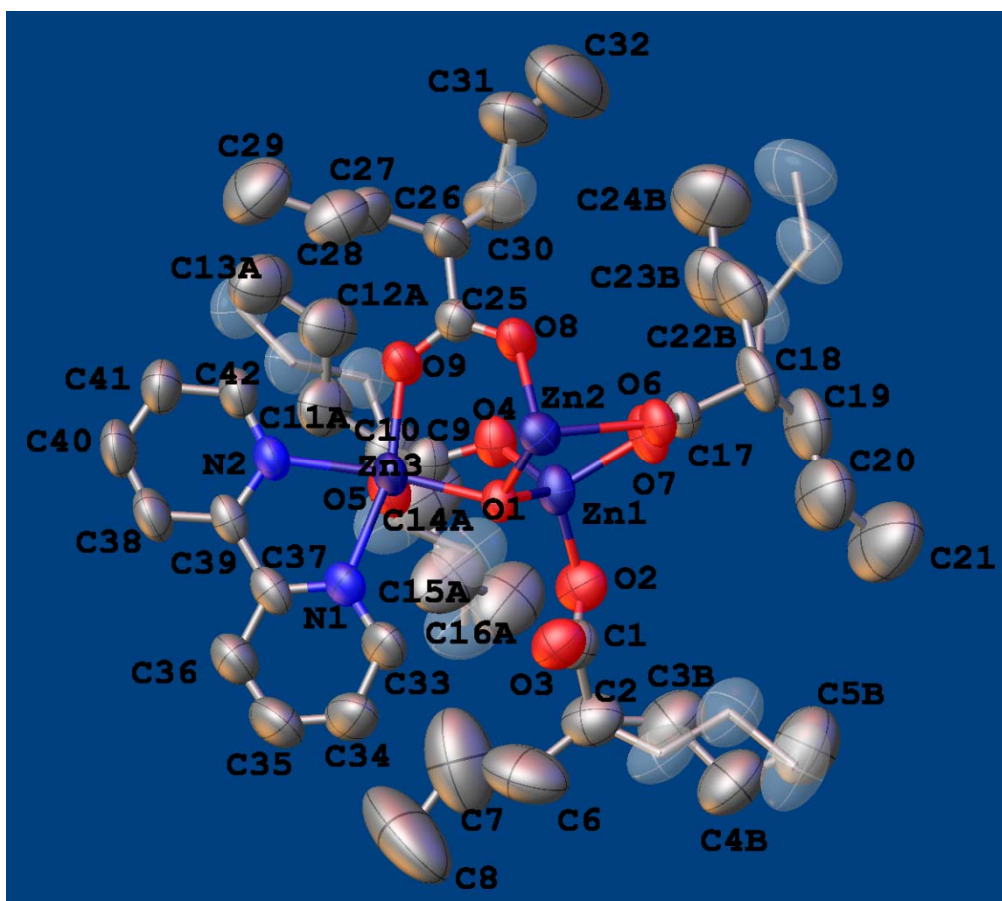




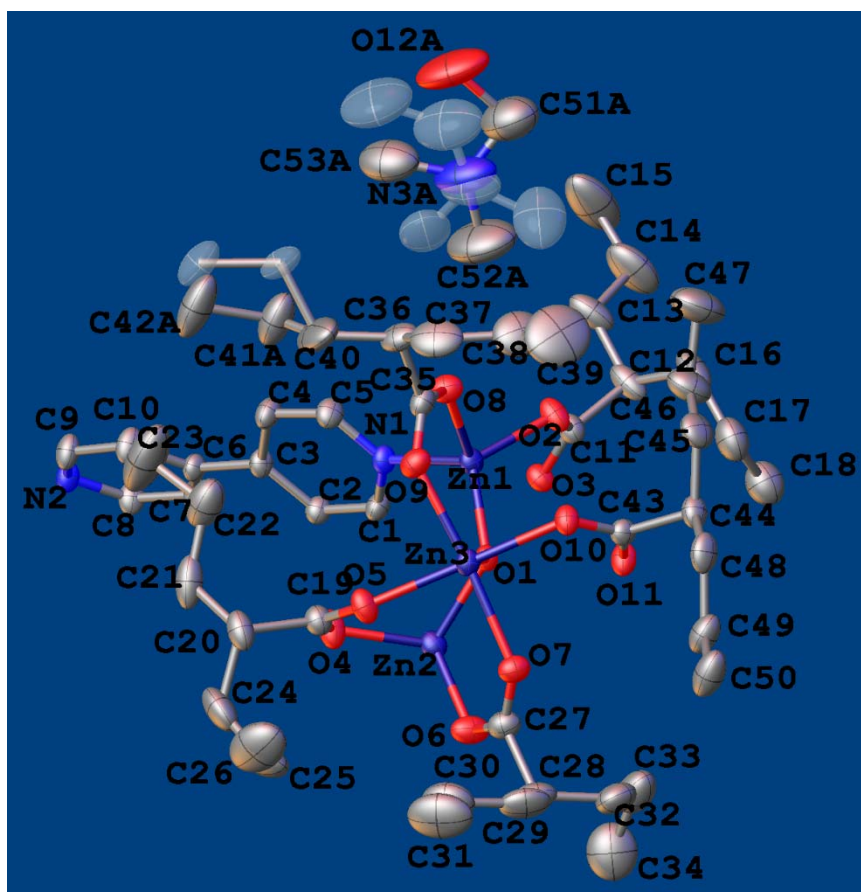
**Figure S7** Hydrophobic surface (branched valproic acid) making well-isolated 2D sheets from the DMF molecules (green) protect clusters (shown as brown polyhedral surface or violet polyhedra) layers.



**Figure S8** (a) Location of DMF molecules as seen along the x axes lying in the central region of the hexagons of the network. The chair conformation of the SBU is seen here too. (b) simplified structure of two alternatives networks along the x axis.



**Figure S9** View of the molecular structure of **II**, showing the atom numbering scheme. Ellipsoids represent thermal displacement parameters at the 50% probability level.



**Figure S10** View of the molecular structure of **III**, showing the atom numbering scheme. Ellipsoids represent thermal displacement parameters at the 50% probability level.

**Table S1** Assignments of the principal IR bands for **I** and sodium valproate ( $\text{cm}^{-1}$ ).

Assignments	NaValp	<b>I</b>
$\nu(\text{C-H})_{\text{aliph}}$	2954 s, 2933 s, 2869 s	2956 s, 2930 s, 2870 m
$\nu_{\text{as}}(\text{COO}^-)$	1548 vs	1594 vs
$\delta(\text{C-H})$	1460 m, 1446 m	1450 s
$\nu_{\text{s}}(\text{COO}^-)$	1411 vs	1426 vs
$\delta(\text{C-H})$	1377 m	1328 s
$\rho(\text{CH}_3)$	1105 m	1120 s
$\delta(\text{COO}^-)$	756 m	757 m
$\pi(\text{COO}^-)$	552 m	524 m
$\rho(\text{COO}^-)$	480 w	475 w
$\Delta_{\nu}(\text{COO}^-)$	137	168

**Table S2** Assignments of selected IR bands for **II<sup>a</sup>** and **III<sup>a</sup>** (cm<sup>-1</sup>).

Assignments	<b>II<sup>a</sup></b>	<b>III<sup>a</sup></b>
$\nu(\text{C-H})_{\text{ar}}$	3077 vw	3052 vw, 3031 vw
$\nu(\text{C-H})_{\text{aliph}}$	2954 s 2930 s 2869 m	2954 s 2931 s 2869 m
$\nu(\text{ring})$	1580 s	1607 s
$\nu_{\text{as}}(\text{COO}^-)$	1551 vs	1572 vs
$\nu(\text{ring}) + \delta(\text{C-H})$	1470 s	1554 s 1470 w
$\nu_{\text{s}}(\text{COO}^-)$	1442 vs	1454 s
$\nu(\text{ring})$	1419 s 1314 s 1225 w 1025 s	1418 vs 1222 s 1070 m 1008 m
$\gamma(\text{C-H})$	864 m 781 vs	865 m 814 vs
$\delta(\text{COO}^-)$	754 m	756 m
$\nu(\text{ring})$	654 m	630 s
$\Delta_{\nu}(\text{COO}^-)$	109	119

**Table S3** UV-Vis spectral data of **I**, **II<sup>a</sup>** and **III<sup>a</sup>**.

Complex	UV-Vis $\lambda_{\text{max}}$ (nm)	$\epsilon$ (extinction coefficient) (M <sup>-1</sup> cm <sup>-1</sup> )
<b>I</b>	- <sup>a</sup>	-
<b>II<sup>a</sup></b>	268 325	12600 5200
<b>III<sup>a</sup></b>	266 364	14100 2600

**a: no bands have been observed.**

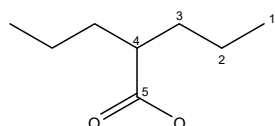


**Table S4**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data for **I**, sodium valproate and valproic acid\*.

H or C No. <sup>a</sup>	$^1\text{H}$ NMR <sup>b</sup> <b>I</b>	$^1\text{H}$ NMR <b>Na<sub>valp</sub></b>	$^{13}\text{C}$ NMR <b>I</b>	$^{13}\text{C}$ NMR <b>Na<sub>valp</sub></b>	$^{13}\text{C}$ NMR <b>H<sub>valp</sub></b>
1	0.87 (t, 6, 7.2)	0.64	14.1	13.3	14.0
2	1.24-1.44 (m, 6)	1.02	20.7	20.5	20.6
3					
4	2.39 (m, 1)	2.01	47.7	48.7	45.2
5			186.1	186.7	183.5

\*ppm downfield relative to TMS as internal standard ( $\text{CDCl}_3$ ).

a: according to the following numbering scheme.



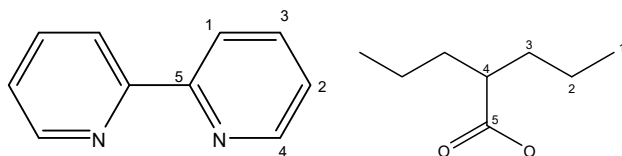
b: the data are chemical shift (multiplicity, integration,  $^3J_{\text{H-H}}$  (Hz)).

**Table S5**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data for **II<sup>a</sup>** and 2,2-bipy\*.

H or C No. <sup>a</sup>	$^1\text{H}$ NMR <sup>b</sup> <b>II<sup>a</sup></b>	$^1\text{H}$ NMR <b>2,2-bipy</b>	$^{13}\text{C}$ NMR <b>II<sup>a</sup></b>	$^{13}\text{C}$ NMR <b>2,2-bipy</b>
1V	0.81 (t, 12, 7.2)		14.2	
2V	1.2-1.41 (m, 12)		20.8	
3V				
4V	2.37 (m, 2)		46.2	
5V			186.3	
1	8.18 (d, 2, 6.9)	8.50	120.9	121.8
2	7.57 (bs, 2)	7.12	126.2	123.6
3	8.0 (bs, 2)	7.66	140.3	136.8
4	9.0 (bs, 2)	8.59	149.9	149.1
5			- <sup>c</sup>	156.1

\*ppm downfield relative to TMS as internal standard ( $\text{CDCl}_3$ ).

a: according to the following numbering scheme (v = valproate)



b: the data are chemical shift (multiplicity, integration,  $^3J_{\text{H-H}}$  (Hz)).

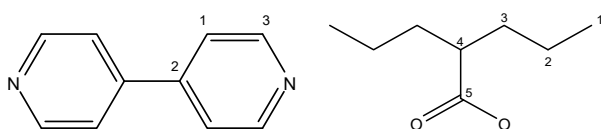
c: not observed mostly because of slow relaxation and the lack of NOE enhancement

**Table S6**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data for **III**<sup>a</sup> and 4,4-bipy\*.

H or C No. <sup>a</sup>	$^1\text{H}$ NMR <sup>b</sup> III <sup>a</sup>	$^1\text{H}$ NMR 4,4-bipy	$^{13}\text{C}$ NMR III <sup>a</sup>	$^{13}\text{C}$ NMR 4,4-bipy
1V	0.855 (t, 12, 7.2)		14.2	
2V	1.21-1.43 (m, 12) 1.56 (m, 4)		20.8	
3V			35.3	
4V	2.38 (m, 2)		47.2	
5V			- <sup>c</sup>	
1	7.58 (dd, 4, 4.8, 1.5)	7.53	121.9	121.4
2			146.3	145.4
3	8.80 (dd, 4, 4.8, 1.5)	8.74	150.6	150.7

\*ppm downfield relative to TMS as internal standard ( $\text{CDCl}_3$ ).

a: according to the following numbering scheme (v = valproate)



b: the data are chemical shift (multiplicity, integration,  $^3J_{\text{H-H}}$  (Hz),  $^4J_{\text{H-H}}$ ).

c: not observed mostly because of slow relaxation and the lack of NOE enhancement.

**Table S7**  $\delta'_{(\text{COO}^-)}$ <sup>b</sup> and  $\Delta_{\text{v}}(\text{COO}^-)$ <sup>c</sup> of **I**, **II**<sup>a</sup> and **III**<sup>a</sup> depending on  $^{13}\text{C}$  NMR and IR data of ( $\text{COO}^-$ ) group

Complex	$\delta_{(\text{CH}_3)}$ <sup>a</sup>	$\delta_{(\text{CH})}$ <sup>a</sup>	$\delta_{(\text{COO}^-)}$ <sup>a</sup>	$\delta'_{(\text{COO}^-)}$ <sup>b</sup>	$\delta'_{(\text{CH})}$ <sup>c</sup>	$\Delta_{\text{v}}(\text{COO}^-)$ <sup>d</sup>
<b>I</b>	14.1	47.7	186.1	172.0	33.6	168
<b>II</b> <sup>a</sup>	14.2	46.2	186.3	172.1	32.0	109
<b>III</b> <sup>a</sup>	14.3	47.2	- <sup>c</sup>	-	33.0	119
<b>H</b> <sub>valp</sub>	13.3	45.2	183.5	170.2	31.2	-
<b>Na</b> <sub>valp</sub>	14.4	48.7	186.7	173.4	35.4	137

a:  $^{13}\text{C}$  chemical shift of  $\text{CH}_3$ ,  $\text{CH}$  and  $\text{COO}^-$  carbons of valproate ligand relative to TMS as internal standard. b:  $^{13}\text{C}$  chemical shift of  $\text{COO}^-$  group of valproate using  $\delta_{(\text{CH}_3)}$  as reference [ $\delta_{(\text{COO}^-)} - \delta_{(\text{CH}_3)}$ ]. c:  $^{13}\text{C}$  chemical shift of  $\text{CH}$  of valproate using  $\delta_{(\text{CH}_3)}$  as reference [ $\delta_{(\text{CH})} - \delta_{(\text{CH}_3)}$ ]. d: [ $\Delta_{\text{v}}(\text{COO}^-) = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$ ], e: not observed.