

## Supporting Information

### Vanadium(III) phenoxyimine complexes for ethylene or $\epsilon$ -caprolactone polymerization: mononuclear *versus* binuclear pre-catalysts

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**Table S1** PPR - Homopolymerization of **S10** and **S12**<sup>a</sup>

Run	Pre-Catalyst (mg)	Metal Content ( $\mu\text{mol}$ ) <sup>b</sup>	Final Ethylene uptake (psi)
1	<b>S10</b> (0.3)	3.17E-03	5.04
2	<b>S10</b> (0.8)	8.44E-03	4.88
3	<b>S10</b> (0.8) <sup>c</sup>	8.44E-03	3.82
4	<b>S12</b> (0.3)	3.17E-03	6.26
5	<b>S12</b> (0.8)	8.44E-03	4.12
6	<b>S12</b> (0.8) <sup>c</sup>	8.44E-03	1.07

<sup>a</sup> **Conditions:** 80°C, 5  $\mu\text{mol}$  TIBA as co-catalyst, 0.5 mol/L ethylene concentration, ethylene pressure: 92 psi, 1 hour polymerization run; reaction quenched with <sup>20</sup> CO<sub>2</sub>; <sup>b</sup> determined by XPS. <sup>c</sup> Repeated Run

**Table S2** PPR - Copolymerization using **S10** and **S12** with TIBA or EADC as co-catalyst<sup>d</sup>

Run	Pro-Catalyst (mg)	Co-catalyst	Metal Content (mmol) <sup>b</sup>	Yield (g)	Activity (g/mmol.hr)	Final Ethylene uptake (psi)
7	<b>S10</b> (0.8)	TIBA	8.44E-06	0.0018	34	2.14
8	<b>S10</b> (1.0)	TIBA	1.06E-05	0.0056	84	4.58
9	<b>S10</b> (0.4)	EADC	4.22E-06	0.0106	396	6.26
10	<b>S10</b> (0.8)	EADC	8.44E-06	0.0215	402	12.21
11	<b>S10</b> (1.0)	EADC	1.06E-05	0.0171	256	10.68
12	<b>S12</b> (0.4)	TIBA	4.22E-06	0.004	150	4.88
13	<b>S12</b> (0.8)	TIBA	8.44E-06	0.0065	121	4.12
14	<b>S12</b> (1.0)	TIBA	1.06E-05	0.0078	117	5.65
15	<b>S12</b> (0.4)	EADC	4.22E-06	0.012	449	5.95
16	<b>S12</b> (0.8)	EADC	8.44E-06	0.0229	428	13.74
17	<b>S12</b> (1.0)	EADC	1.06E-05	0.0178	266	14.35

<sup>a</sup> **Conditions:** 80°C, 5  $\mu\text{mol}$  TIBA as co-catalyst, 0.5 mol/L ethylene concentration, ethylene pressure: 92 psi, 1 hour polymerization run; reaction quenched with <sup>25</sup> CO<sub>2</sub>; <sup>b</sup> determined by XPS; metal content was 0.0537% of bulk sample.

**Table S3** PPR - Copolymerization using **S10** or **S12** with co-catalyst EADC and ETA<sup>a</sup>.

Run	Pro-Catalyst (mg)	Metal Content (mmol) <sup>b</sup>	Yield (g)	Activity (g/mmol.hr)	Final Ethylene uptake (psi)	ETA:M Ratio
18	<b>S10</b> (0.3)	3.17E-06	0.0054	269	10.38	1440
19	<b>S10</b> (0.3) <sup>c</sup>	3.17E-06	0.0152	757	16.03	1440
20	<b>S10</b> (0.8)	8.44E-06	0.0017	32	3.51	1440
21	<b>S10</b> (0.8) <sup>c</sup>	8.44E-06	0.0038	71	5.04	1440
22	<b>S12</b> (0.3)	3.17E-06	0.0288	1435	18.77	720
23	<b>S12</b> (0.3)	3.17E-06	0.004	199	8.09	1440
24	<b>S12</b> (0.3) <sup>c</sup>	3.17E-06	0.0085	424	7.94	1440
25	<b>S12</b> (0.3) <sup>c</sup>	3.17E-06	0.035	1744	25.64	1440
26	<b>S12</b> (0.3) <sup>c</sup>	3.17E-06	0.0125	623	11.14	1440
27	<b>S12</b> (0.8)	8.44E-06	0.0086	161	10.38	1440
28	<b>S12</b> (0.8) <sup>c</sup>	8.44E-06	0.0081	151	8.70	1440

<sup>a</sup> **Conditions:** 80°C, 5 μmol EADC as co-catalyst, 0.5 mol/L ethylene concentration, ethylene pressure: 92 psi, 1 hour polymerization run; ETA added as a solution in heptane; reaction quenched with CO<sub>2</sub>; <sup>b</sup> determined by XPS: metal content was 0.0537% of bulk sample; <sup>c</sup> repeated runs.