Electronic Supplementary Information (ESI)

# Synthesis and Structural Analysis of Tungsten-Carbonyl Dimers Bridged with Oligo(2,5-dialkoxy-1,4-phenylene vinylene)s through Pyridine Coordination

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NMR and IR spectra for (a) **[W(CO)$_5$]$_2$-Bpy** (**1**), (b) **[W(CO)$_5$]$_2$-(1PV-Py$_2$)** (**2**), (c) **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**).

Molecular packings of (a) **[W(CO)$_5$]$_2$-Bpy** (**1**), (b) **[W(CO)$_5$]$_2$-(1PV-Py$_2$)** (**2**), (c) **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**) in the crystal unit cell.

Disordered O, Si, and C atoms of OSi(*i*-Pr)$_3$ groups in **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**). A table describing the detail parameters including the occupancy of each atoms.

CIF files for **[W(CO)$_5$]-Bpy** (**1**), **[W(CO)$_5$]-(1PV-Py$_2$)** (**2**), and **[W(CO)$_5$]-(3PV-Py$_2$)** (**3**), deposited as CCDC1409638-1409640.

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1-1. NMR spectra for **$[W(CO)_5]_2$-Bpy** (**1**), **$[W(CO)_5]_2$-(1PV-$Py_2$)** (**2**), and **$[W(CO)_5]_2$-(3PV-$Py_2$)** (**3**).

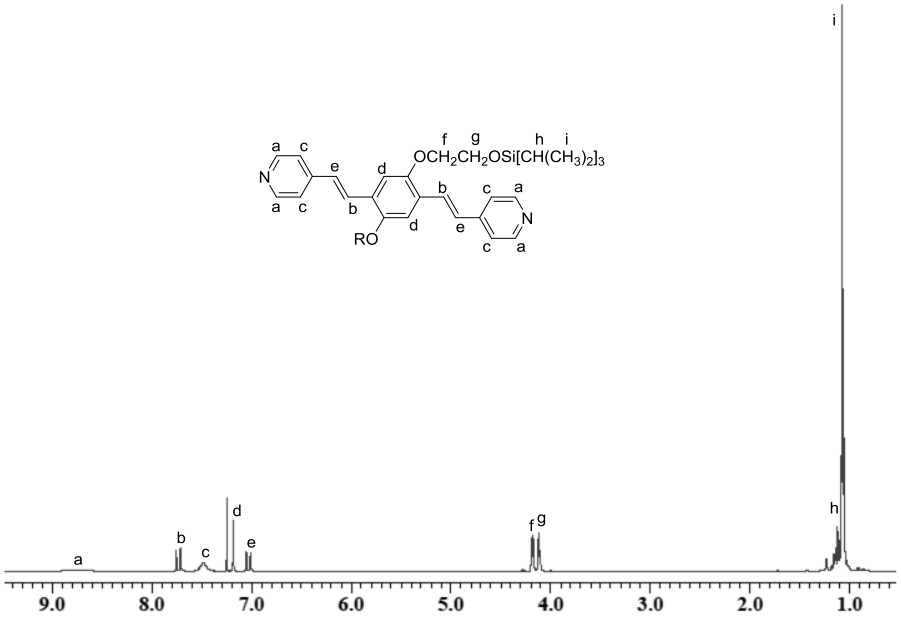


**Figure S1-1.** $^1$H NMR spectrum (in $CDCl_3$ at 25 ºC) of **1PV-$Py_2$.**

$^1$H NMR ($CDCl_3$ at 25 ºC): $\delta$ 8.77 (br, 4H), 7.74 (d, 2H), 7.49 (br, 4H), 7.20 (s, 2H), 7.04 (d, 2H), 4.20 (t, 4H), 4.13 (t, 4H), 1.13 (m, 6H), 1.08 (d, 36H).

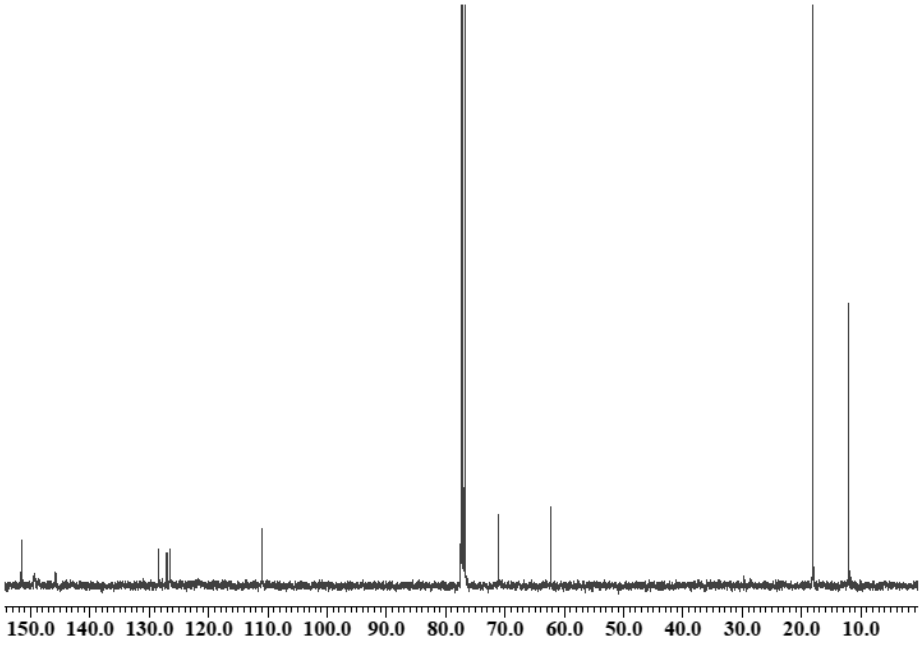


**Figure S1-2.** $^{13}$C NMR spectrum (in $CDCl_3$ at 25 ºC) of **1PV-$Py_2$.**

$^{13}$C NMR ($CDCl_3$ at 25 ºC): $\delta$ 151.5, 149.3, 145.7, 131.0, 128.3, 127.0, 126.4, 110.8, 71.0, 62.3, 18.0, 12.0.

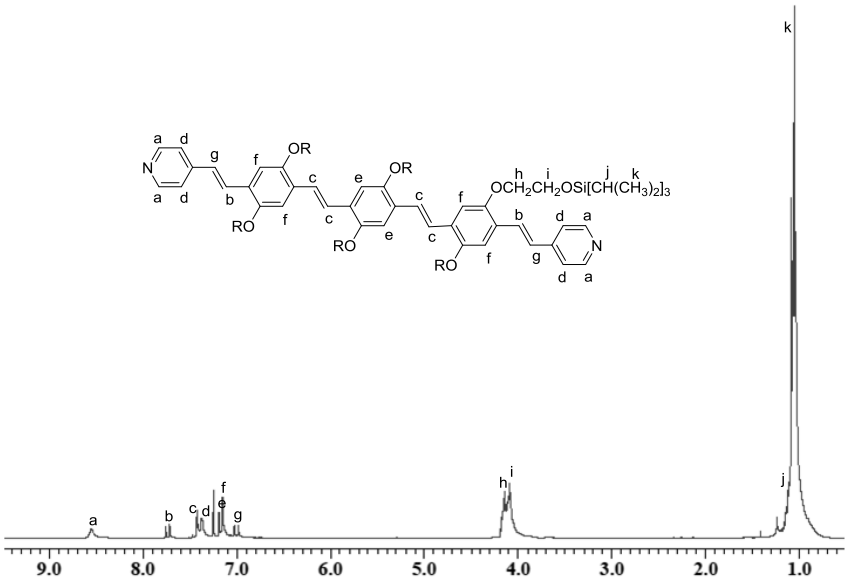


**Figure S1-3.** $^{1}$H NMR spectrum (in $CDCl_3$ at 25 ºC) of **3PV-Py$_2$**.

$^{1}$H NMR ($CDCl_3$ at 25 ºC): $\delta$ 8.56 (br, 4H), 7.75 (d, 2H), 7.43 (m, 4H), 7.39 (br, 4H), 7.20 (s, 2H), 7.16 (s, 4H), 7.01 (d, 2H), 4.16 (m, 12H), 4.10 (m, 12H), 1.12 (m, 18H), 1.06 (m, 108H).

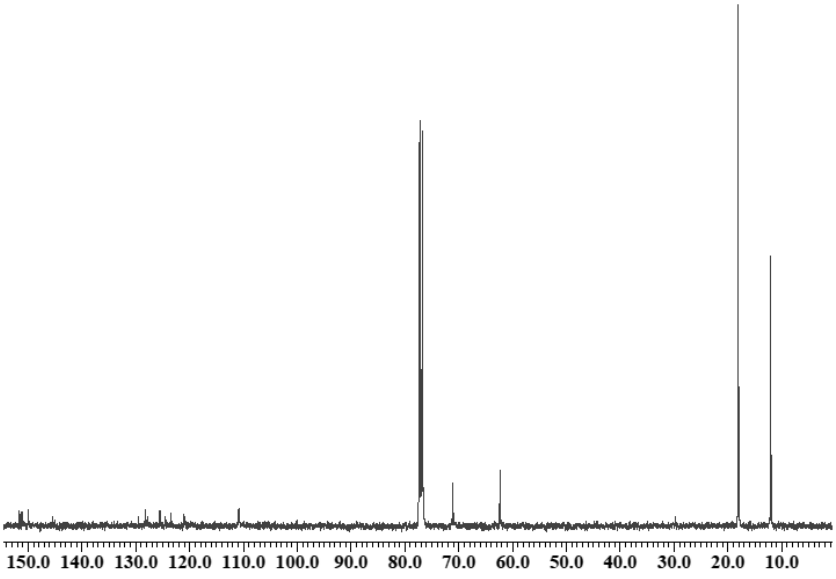


**Figure S1-4.** $^{13}$C NMR spectrum (in $CDCl_3$ at 25 ºC) of **3PV-Py$_2$**.

$^{13}$C NMR ($CDCl_3$ at 25 ºC): $\delta$ 151.5, 151.1, 150.9, 149.9, 145.4, 130.7, 129.4, 128.1, 127.8, 125.5, 124.4, 123.4, 120.9, 110.8, 71.0, 62.3, 18.0, 12.0.

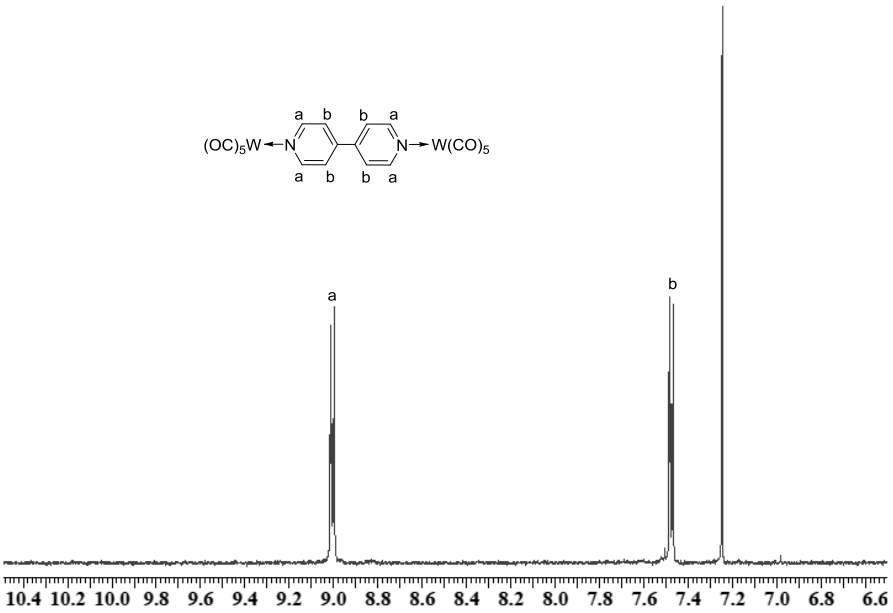


**Figure S1-5.** $^{1}$H NMR spectrum (in $CDCl_3$ at 25 ºC) of **$[W(CO)_5]_2$-Bpy**.

$^{1}$H NMR ($CDCl_3$ at 25 ºC): $\delta$ 9.02 (d, 4H), 7.49 (d, 4H).

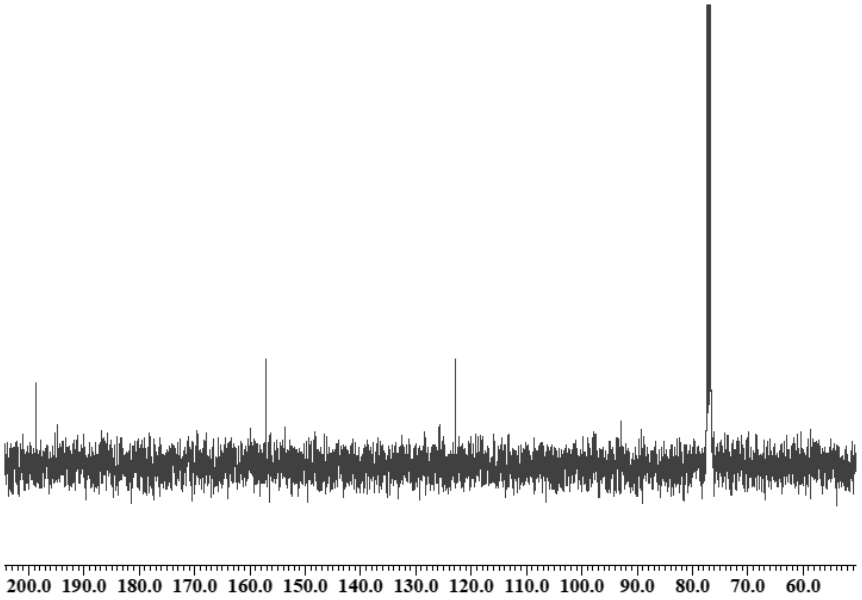


**Figure S1-6.** $^{13}$C NMR spectrum (in $CDCl_3$ at 25 ºC) of **$[W(CO)_5]_2$-Bpy**.

$^{13}$C NMR ($CDCl_3$ at 25 ºC): $\delta$ 198.6, 157.1, 122.8.

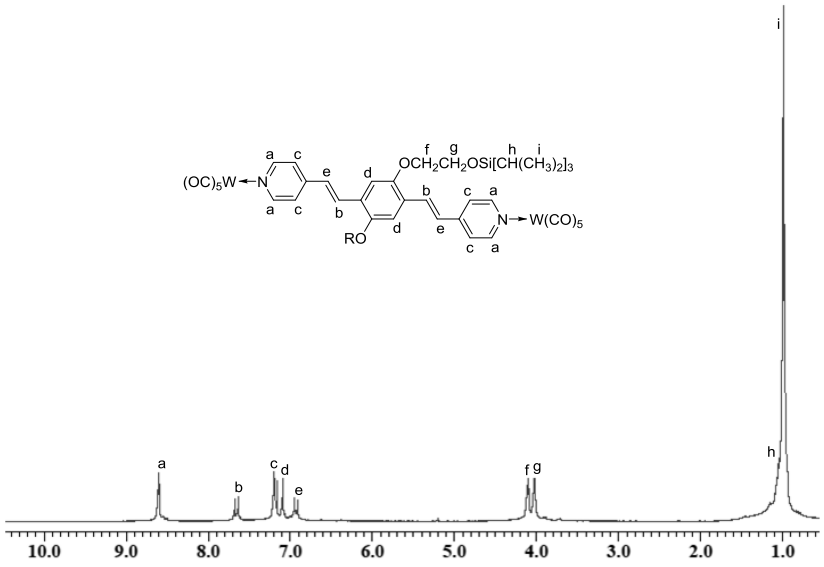


**Figure S1-7.** $^{1}$H NMR spectrum (in $CDCl_3$ at 25 ºC) of **$[W(CO)_5]_2$-(1PV-$Py_2$)**.

$^{1}$H NMR ($CDCl_3$ at 25 ºC): $\delta$ 8.70 (d, 4H), 7.75 (d, 2H), 7.29 (d, 4H), 7.19 (s, 2H), 7.03 (d, 2H), 4.21 (t, 4H), 4.12 (t, 4H), 1.14 (m, 6H), 1.09 (d, 36H).

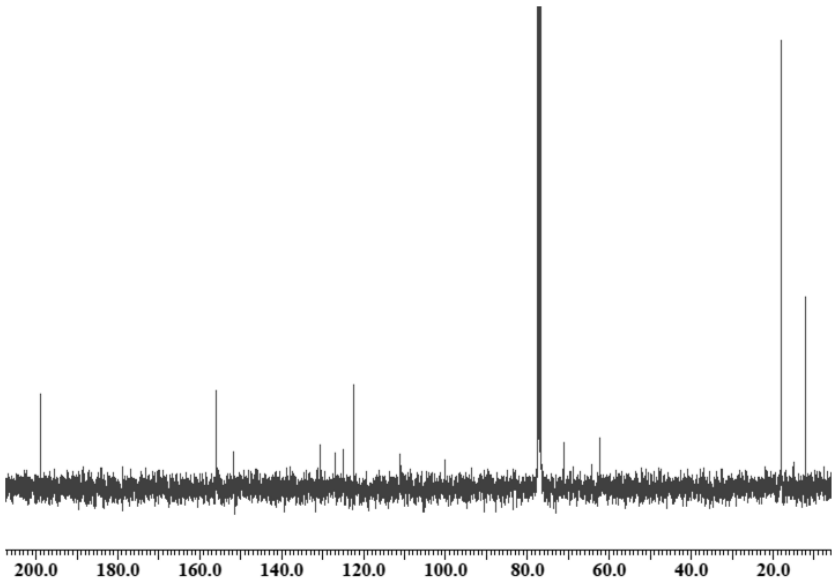


**Figure S1-8.** $^{13}$C NMR spectrum (in $CDCl_3$ at 25 ºC) of **$[W(CO)_5]_2$-(1PV-$Py_2$)**.

$^{13}$C NMR ($CDCl_3$ at 25 ºC): $\delta$ 198.9, 155.9, 151.8, 130.4, 126.9, 124.9, 122.3, 111.7, 99.8, 71.1, 62.2, 18.0, 12.0.

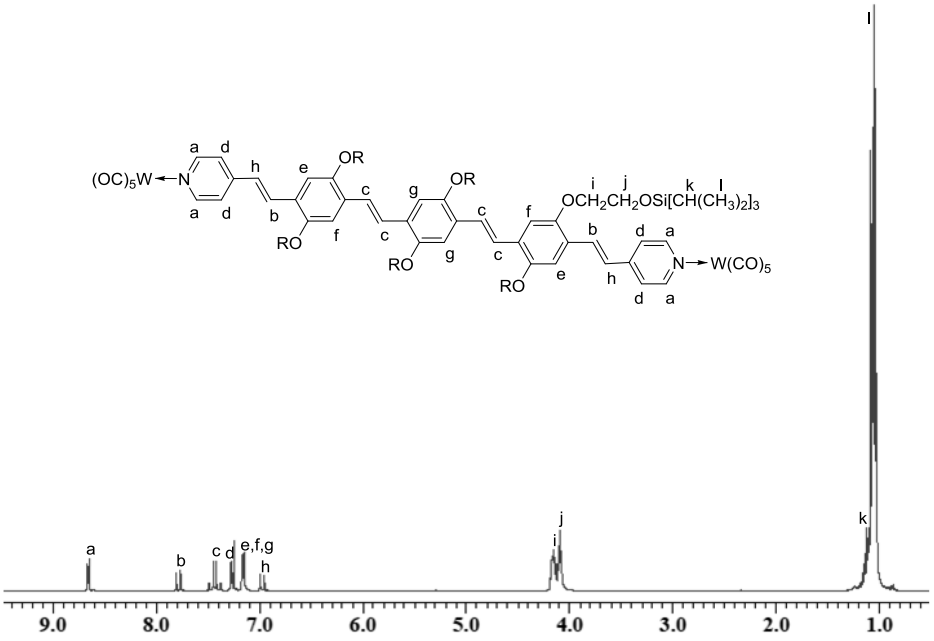


**Figure S1-9.** $^{1}$H NMR spectrum (in $CDCl_3$ at 25 ºC) of **$[W(CO)_5]_2$-(3PV-$Py_2$)**.

$^{1}$H NMR ($CDCl_3$ at 25 ºC): $\delta$ 8.67 (d, 4H), 7.80 (d, 2H), 7.47 (d, 2H), 7.42 (d, 2H), 7.28 (d, 4H), 7.18 (s, 2H), 7.17 (s, 2H), 7.16 (s, 2H), 6.98 (d, 2H), 4.18 (m, 12H), 4.09 (m, 12H), 1.13 (m, 18H), 1.08 (m, 108H).

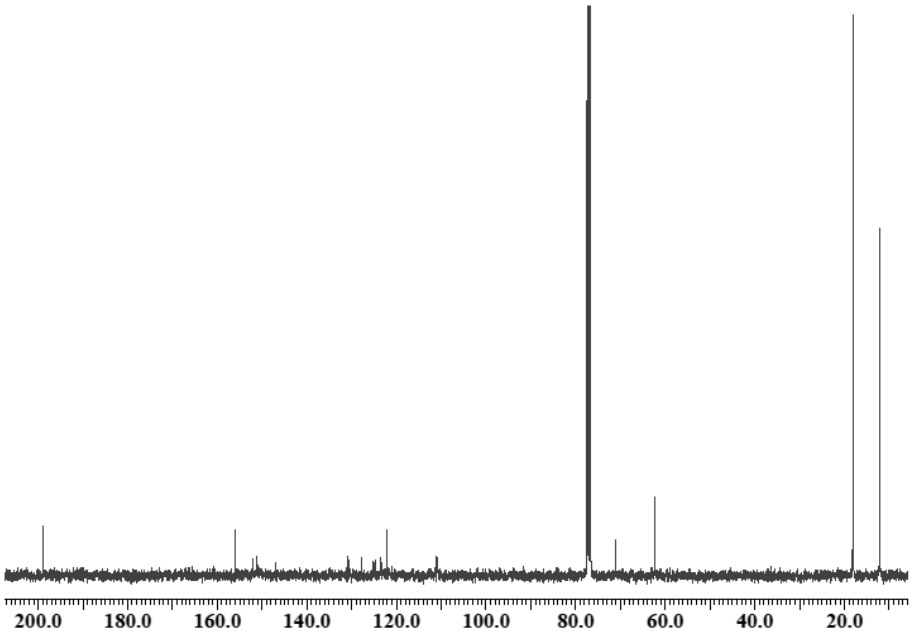


**Figure S1-10.** $^{13}$C NMR spectrum (in $CDCl_3$ at 25 ºC) of **$[W(CO)_5]_2$-(3PV-$Py_2$)**.

$^{13}$C NMR ($CDCl_3$ at 25 ºC): $\delta$ 198.9, 155.8, 151.9, 151.1, 151.0, 146.9, 130.9, 130.4, 127.8, 125.2, 125.0, 124.5, 123.4, 122.2, 110.8, 71.0, 62.3, 18.0, 12.0.

1-2. IR spectra for **$[W(CO)_5]_2$-Bpy** (**1**), **$[W(CO)_5]_2$-(1PV-$Py_2$)** (**2**), and **$[W(CO)_5]_2$-(3PV-$Py_2$)** (**3**).

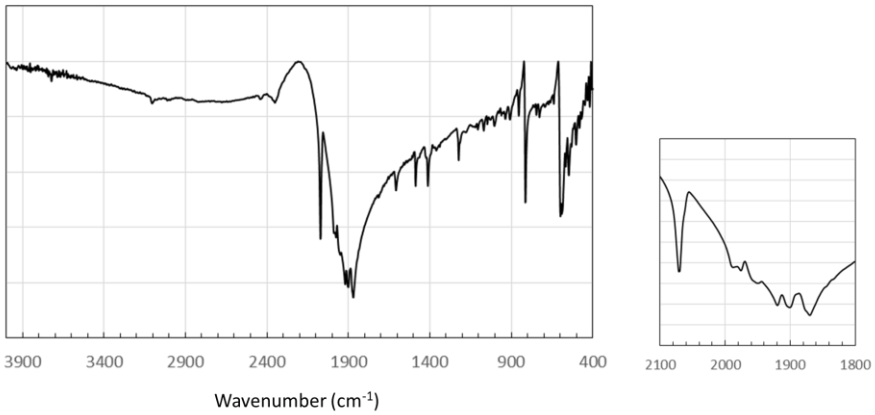


**Figure S1-11**. FT-IR spectrum for **$[W(CO)_5]_2$-Bpy** (**1**). IR (KBr) ($cm^{-1}$): 2072 (m) $\nu_{CO}$, 1975 (w) $\nu_{CO}$, 1950 (w) $\nu_{CO}$, 1919 (s) $\nu_{CO}$, 1900 (s) $\nu_{CO}$, 1869 (s) $\nu_{CO}$.

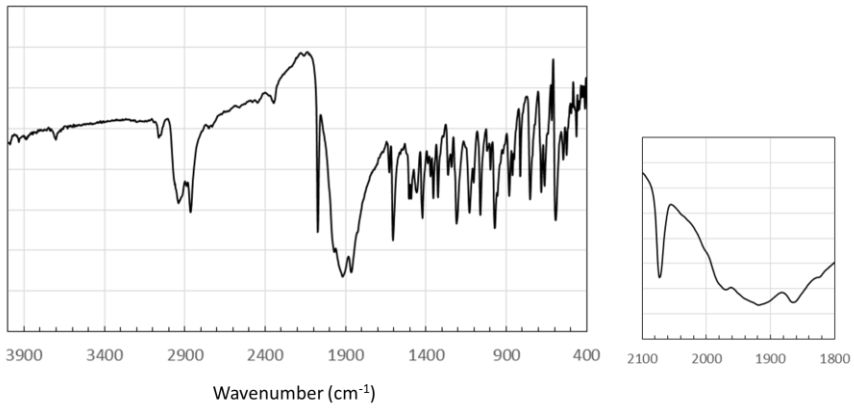


**Figure S1-12**. FT-IR spectrum for **$[W(CO)_5]_2$-(1PV-$Py_2$)** (**2**). IR (KBr) ($cm^{-1}$): 2073 (m) $\nu_{CO}$, 1969 (w) $\nu_{CO}$, 1919 (s, br) $\nu_{CO}$, 1865 (s) $\nu_{CO}$.

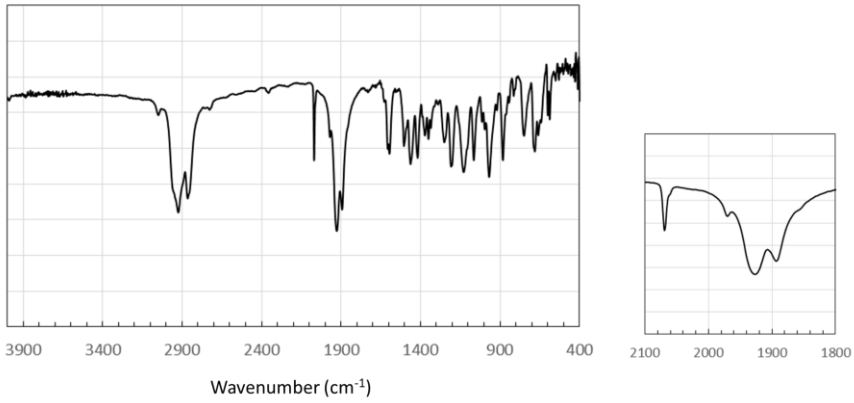


**Figure S1-13**. FT-IR spectrum for **$[W(CO)_5]_2$-(3PV-$Py_2$)** (**3**). IR (KBr) ($cm^{-1}$): 2070 (m) $\nu_{CO}$, 1969 (w) $\nu_{CO}$, 1927 (s, br) $\nu_{CO}$, 1894 (s) $\nu_{CO}$.

2. Additional figures and table for explanation (crystallographic analysis).

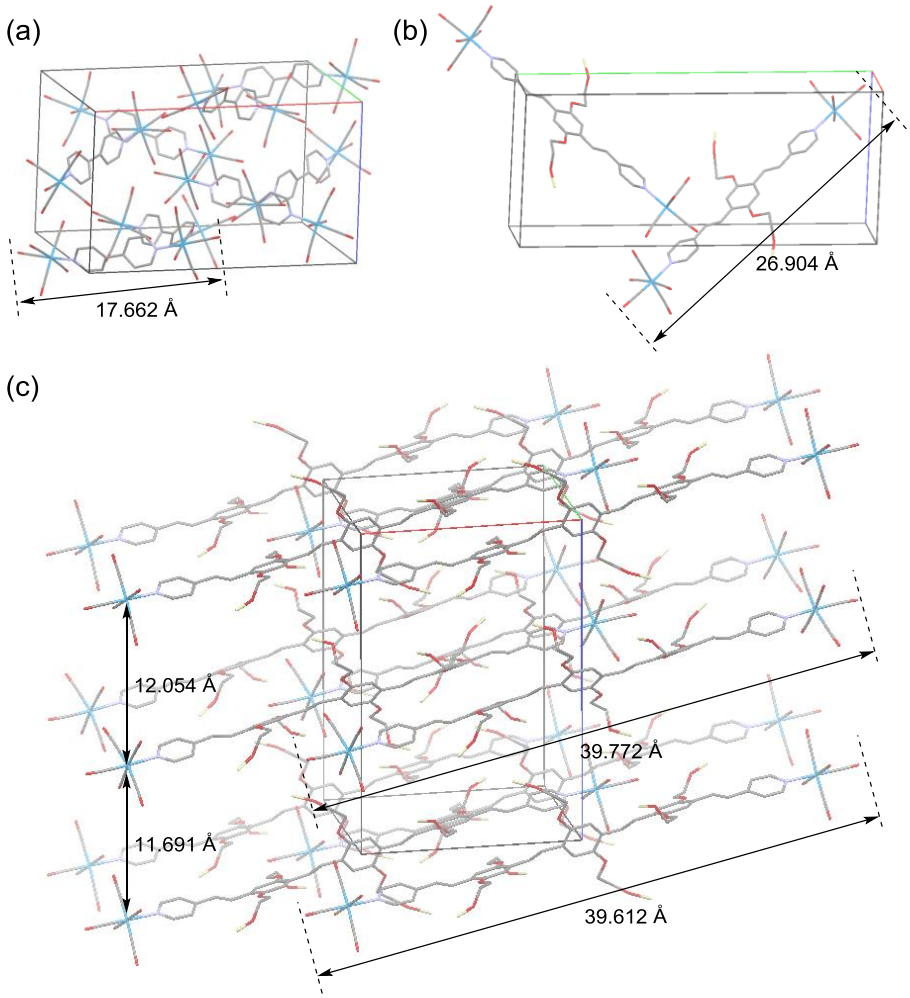


**Figure S2**. Molecular packings of (a) **$[W(CO)_5]_2$-Bpy** (**1**), (b) **$[W(CO)_5]_2$-(1PV-$Py_2$)** (**2**), (c) **$[W(CO)_5]_2$-(3PV-$Py_2$)** (**3**) in the crystal unit cell. H atoms and isopropyl groups are omitted for clarity.

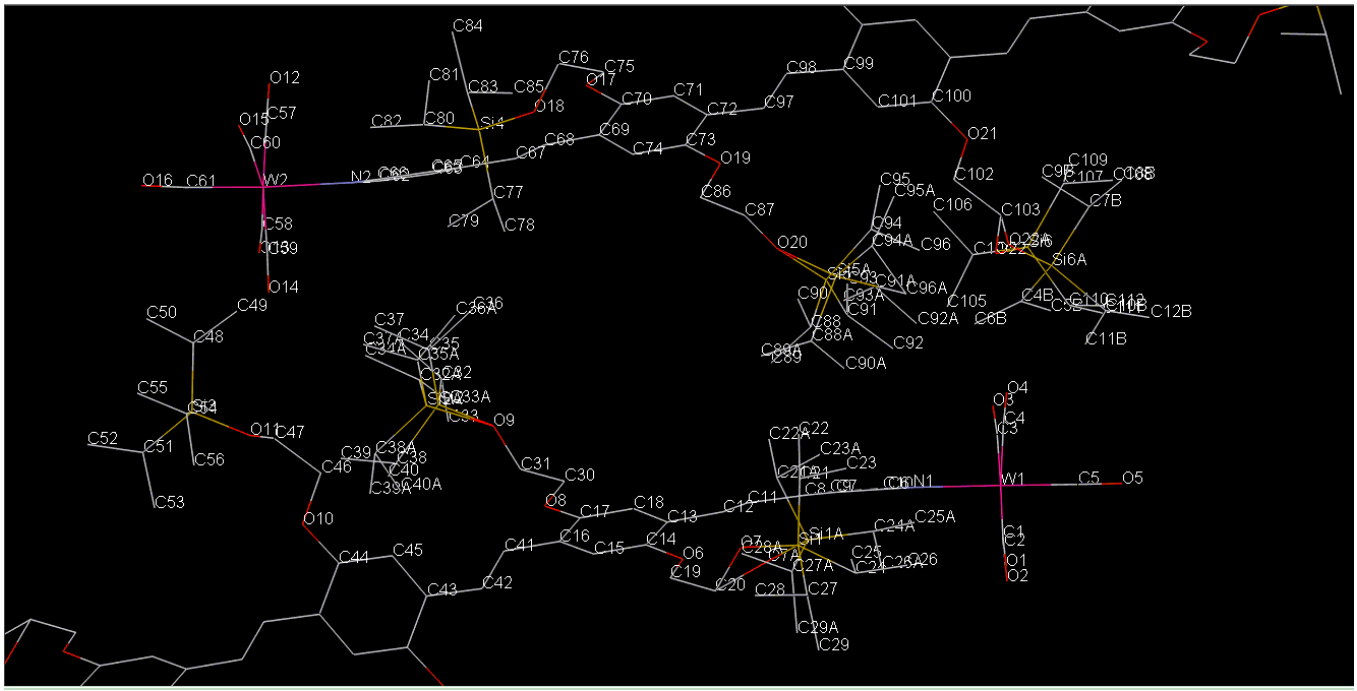


**Figure S3**. Disordered O, Si, and C atoms of OSi(*i*-Pr)$_3$ groups in **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**). The detail parameters including the occupancy of each atoms were shown in Table S1 (next page).

**Table S1**. Atomic coordinates and $B_{iso}/B_{eq}$ and occupancy

| atom | x | y | z | $B_{eq}$ | occ |
|---|---|---|---|---|---|
| C24 | 0.7638(13) | -0.5047(11) | 0.0829(11) | 8.7(4) | 0.632(13) |
| C25 | 0.783(2) | -0.4274(15) | 0.0786(17) | 12.3(8) | 0.632(13) |
| C26 | 0.8395(17) | -0.5733(15) | 0.1007(12) | 9.7(6) | 0.632(13) |
| Si1 | 0.6483(9) | -0.5019(9) | 0.1240(6) | 6.8(2) | 0.632(13) |
| O7 | 0.5651(12) | -0.4219(8) | 0.1105(6) | 7.2(3) | 0.632(13) |
| C27 | 0.6363(16) | -0.5895(12) | 0.0916(9) | 8.3(4) | 0.632(13) |
| C28 | 0.5316(17) | -0.5926(15) | 0.1019(11) | 8.8(5) | 0.632(13) |
| C29 | 0.668(2) | -0.5797(17) | 0.0251(10) | 10.5(6) | 0.632(13) |
| C21 | 0.636(2) | -0.5285(11) | 0.2049(8) | 8.4(4) | 0.632(13) |
| C22 | 0.654(3) | -0.4685(16) | 0.2381(13) | 12.2(8) | 0.632(13) |
| C23 | 0.697(2) | -0.6082(14) | 0.2294(11) | 11.1(8) | 0.632(13) |
| C21A | 0.603(3) | -0.496(2) | 0.2012(12) | 8.5(5) | 0.368(13) |
| C22A | 0.612(3) | -0.424(3) | 0.225(2) | 9.7(8) | 0.368(13) |
| C23A | 0.659(4) | -0.568(3) | 0.239(2) | 11.1(10) | 0.368(13) |
| C27A | 0.609(2) | -0.577(2) | 0.1172(16) | 8.3(5) | 0.368(13) |
| C28A | 0.508(2) | -0.575(3) | 0.146(2) | 9.9(8) | 0.368(13) |
| C29A | 0.614(3) | -0.603(3) | 0.0548(18) | 9.2(7) | 0.368(13) |
| O7A | 0.6221(17) | -0.4144(14) | 0.0877(13) | 8.3(5) | 0.368(13) |
| Si1A | 0.6682(13) | -0.4986(16) | 0.1273(11) | 6.7(3) | 0.368(13) |
| C24A | 0.7964(16) | -0.5024(19) | 0.1253(16) | 8.3(6) | 0.368(13) |
| C25A | 0.847(2) | -0.582(2) | 0.149(2) | 10.2(11) | 0.368(13) |
| C26A | 0.832(3) | -0.463(2) | 0.0714(16) | 7.8(7) | 0.368(13) |
| Si2 | 0.2135(6) | 0.2579(4) | 0.1384(4) | 3.18(11) | 0.645(17) |
| C38 | 0.1382(12) | 0.2694(9) | 0.0782(8) | 5.9(3) | 0.645(17) |
| C39 | 0.0549(13) | 0.3396(11) | 0.0747(11) | 8.0(5) | 0.645(17) |
| C40 | 0.096(2) | 0.1971(15) | 0.0854(17) | 9.1(8) | 0.645(17) |
| C35 | 0.1737(9) | 0.2148(9) | 0.2127(6) | 4.2(3) | 0.645(17) |
| C36 | 0.2514(12) | 0.1960(13) | 0.2548(8) | 4.7(3) | 0.645(17) |

| | | | | | |
|---|---|---|---|---|---|
| C37 | 0.0789(13) | 0.2571(14) | 0.2383(9) | 7.3(5) | 0.645(17) |
| C32 | 0.2525(11) | 0.3488(7) | 0.1417(6) | 4.4(3) | 0.645(17) |
| C33 | 0.2839(17) | 0.3859(12) | 0.0813(8) | 5.2(4) | 0.645(17) |
| C34 | 0.1866(13) | 0.4088(9) | 0.1755(8) | 6.0(4) | 0.645(17) |
| C32A | 0.214(2) | 0.3633(17) | 0.140(2) | 7.2(6) | 0.355(17) |
| C33A | 0.288(4) | 0.396(3) | 0.101(2) | 8.6(11) | 0.355(17) |
| C34A | 0.121(3) | 0.407(3) | 0.166(2) | 10.4(11) | 0.355(17) |
| C35A | 0.150(2) | 0.210(2) | 0.2051(14) | 6.9(5) | 0.355(17) |
| C36A | 0.219(2) | 0.202(3) | 0.2505(19) | 6.2(7) | 0.355(17) |
| C37A | 0.069(3) | 0.282(3) | 0.213(2) | 9.9(9) | 0.355(17) |
| C39A | 0.1091(19) | 0.3221(19) | 0.0346(13) | 6.3(5) | 0.355(17) |
| C40A | 0.119(3) | 0.192(2) | 0.069(3) | 5.7(6) | 0.355(17) |
| C38A | 0.096(2) | 0.2710(17) | 0.0930(13) | 6.8(5) | 0.355(17) |
| Si2A | 0.1928(15) | 0.2655(13) | 0.1375(11) | 5.9(4) | 0.355(17) |
| Si6 | 1.2348(4) | -0.1031(3) | 0.3001(3) | 3.60(11) | 0.538(9) |
| O22 | 1.1536(9) | -0.1495(10) | 0.3117(5) | 5.2(3) | 0.538(9) |
| C110 | 1.3062(13) | -0.1442(11) | 0.2389(9) | 4.9(3) | 0.538(9) |
| C111 | 1.345(3) | -0.2191(19) | 0.245(2) | 7.4(6) | 0.538(9) |
| C112 | 1.3923(14) | -0.1032(14) | 0.2203(9) | 6.0(4) | 0.538(9) |
| C107 | 1.3007(10) | -0.1050(9) | 0.3640(6) | 3.6(2) | 0.538(9) |
| C108 | 1.370(2) | -0.1787(15) | 0.3786(18) | 4.2(4) | 0.538(9) |
| C109 | 1.3333(12) | -0.0392(10) | 0.3648(6) | 3.6(3) | 0.538(9) |
| C104 | 1.1657(11) | -0.0009(9) | 0.2738(7) | 4.4(3) | 0.538(9) |
| C105 | 1.1200(14) | 0.0023(11) | 0.2201(9) | 4.9(4) | 0.538(9) |
| C106 | 1.0962(12) | 0.0338(10) | 0.3203(8) | 5.0(3) | 0.538(9) |
| Si6A | 1.2748(6) | -0.1257(5) | 0.2812(4) | 5.61(17) | 0.462(9) |
| O22A | 1.1805(12) | -0.1466(13) | 0.3180(6) | 5.7(3) | 0.462(9) |
| C10B | 1.343(4) | -0.239(2) | 0.252(3) | 7.3(5) | 0.462(9) |
| C11B | 1.296(3) | -0.260(2) | 0.2243(17) | 10.1(8) | 0.462(9) |
| C12B | 1.439(2) | -0.2198(18) | 0.2307(15) | 8.4(7) | 0.462(9) |
| C7B | 1.3507(16) | -0.1116(15) | 0.3353(10) | 5.8(4) | 0.462(9) |
| C8B | 1.390(3) | -0.179(2) | 0.378(3) | 6.7(8) | 0.462(9) |

| | | | | | |
|---|---|---|---|---|---|
| C9B | 1.291(2) | -0.016(2) | 0.3511(17) | 8.6(7) | 0.462(9) |
| C4B | 1.251(2) | -0.0367(18) | 0.2228(13) | 7.6(5) | 0.462(9) |
| C6B | 1.172(2) | -0.007(2) | 0.1984(18) | 9.6(9) | 0.462(9) |
| C5B | 1.324(2) | -0.0041(18) | 0.1975(13) | 7.7(6) | 0.462(9) |
| Si5 | 0.7843(6) | -0.2392(5) | 0.3401(4) | 4.54(13) | 0.656(11) |
| C88 | 0.7324(15) | -0.3043(11) | 0.3086(8) | 7.6(4) | 0.656(11) |
| C89 | 0.678(2) | -0.246(2) | 0.2599(14) | 11.5(8) | 0.656(11) |
| C90 | 0.6852(18) | -0.3551(13) | 0.3564(10) | 9.4(6) | 0.656(11) |
| C94 | 0.8476(12) | -0.2982(9) | 0.4037(7) | 6.0(3) | 0.656(11) |
| C95 | 0.8809(15) | -0.2476(14) | 0.4368(10) | 8.2(5) | 0.656(11) |
| C96 | 0.9178(15) | -0.3722(12) | 0.3914(10) | 8.9(6) | 0.656(11) |
| C91 | 0.8492(13) | -0.1865(10) | 0.2823(7) | 6.8(3) | 0.656(11) |
| C92 | 0.9225(18) | -0.2390(18) | 0.2511(12) | 10.1(6) | 0.656(11) |
| C93 | 0.873(2) | -0.1184(13) | 0.2983(10) | 6.6(5) | 0.656(11) |
| Si5A | 0.8053(15) | -0.2354(15) | 0.3410(11) | 6.8(4) | 0.344(11) |
| C88A | 0.7523(19) | -0.258(2) | 0.2802(16) | 7.4(5) | 0.344(11) |
| C89A | 0.652(2) | -0.260(3) | 0.274(2) | 6.3(7) | 0.344(11) |
| C90A | 0.789(3) | -0.343(2) | 0.266(2) | 9.4(9) | 0.344(11) |
| C94A | 0.839(3) | -0.3275(19) | 0.3933(14) | 8.2(5) | 0.344(11) |
| C95A | 0.888(3) | -0.306(3) | 0.4383(18) | 9.0(8) | 0.344(11) |
| C96A | 0.895(3) | -0.368(3) | 0.3451(19) | 9.3(6) | 0.344(11) |
| C91A | 0.9005(16) | -0.1908(15) | 0.3096(12) | 5.4(4) | 0.344(11) |
| C92A | 0.966(3) | -0.247(3) | 0.2758(19) | 7.7(8) | 0.344(11) |
| C93A | 0.869(4) | -0.1102(19) | 0.278(2) | 6.6(8) | 0.344(11) |

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$