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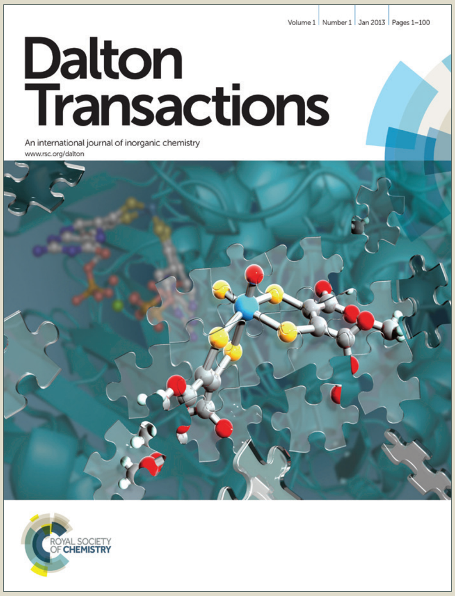

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ARTICLE

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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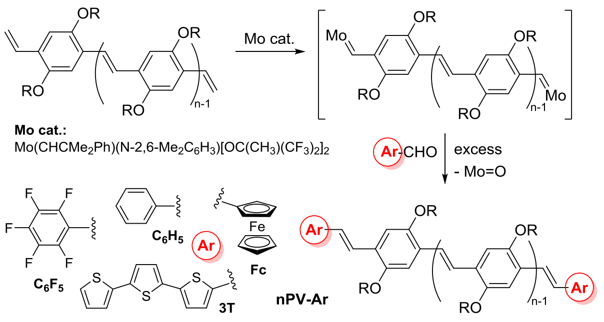
Tungsten carbonyl dimers bridged with oligo(2,5-dialkoxy-1,4-phenylene vinylene)s through coordination with pyridine as the end groups, expressed as **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** [n = 1, 3; alkoxy = O(CH$_2$)$_2$OSi^{i}Pr$_3$], have been prepared from W(CO)$_5$(THF) with ***n*PV-Py$_2$** in THF, and their structures were determined by X ray crystallography. Both increase in absorbance and redshift in the λ_{max} values in **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** from their ***n*PV-Py$_2$** were observed in the UV-vis spectra, due to increase in the conjugation length through tungsten by coordination of pyridine moiety; an extension of the conjugation was also confirmed by the crystallographic analysis as well as fluorescence spectra.

Introduction

Organic electronics have been recognized as important emerging technologies, and conjugated polymers/oligomers are promising semiconducting materials.[1-4] Since control of structural regularity, chemical purity, and supramolecular order[2,3] are important factors for the better performances, development of new synthetic methods/methodology for the efficient synthesis thus attracts considerable attention.[1] Oligo(*p*-phenylene vinylene)s (OPVs) are one of the most studied π-conjugated molecules due to their promising optoelectronic properties.[5-8] The end-group modification has been known as an alternative, versatile approach that facilitates the electronic nature through a more efficient intramolecular charge transfer;[5-8] certain EF-OPVs are known to act as π-gelators[5b,d,e,6,7c] and optically active OPVs are generated through hydrogen bonding by chiral additives[7a,b,d] or by introduction of the chiral alkoxy end groups.[7c] However, examples for synthesis of a series of well-defined (structurally regular) end-functionalized OPVs (EF-OPVs) are still limited.[5-8] We recently demonstrated precise synthesis of analytically pure oligo(2,5-dialkoxy-1,4-phenylene vinylene)s [alkoxy = O(CH$_2$)$_2$OSi^{i}Pr$_3$] with strictly controlled repeat units (up to 31 repeat units), well-defined end groups (CHO etc.), by adopting combined olefin metathesis and Wittig-type coupling;[8] introductions of several end groups (shown in Scheme 1) could be achieved by adopting this synthetic strategy. This can be achieved by treating the vinyl groups with Mo-alkylidene (**Mo** cat.) followed by Wittig-type cleavage with aldehyde,[9] as first demonstrated by poly(9,9-dialkylfluorene-2,7-vinylene)s (PFVs) prepared by acyclic diene metathesis (ADMET) polymerization using ruthenium catalysts.[10,11]



Scheme 1. Synthesis of end-functionalized oligo(phenylene vinylene)s (EF-OPV)s by olefin metathesis and Wittig coupling.[8]

Transition metal complexes are powerful templates for organizing organic chromophores with coordinating termini into well-defined supramolecular assemblies.[12-15] Although OPV was also used as linkers,[14] examples for the use of substituted (especially alkoxy-substituted) OPVs, which are known to exhibit promising characteristics as molecular electronics, have been limited so far. It has been expected that synthesis and structural analysis of these oligomers by isolation as transition metal complexes (including basic analysis of optical properties) would provide new information for better basic understanding (structural information including specific self-assembly in nano scale etc.) as well as for design of better molecular devices.[1,5,6] Since the method adopted here enables

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Electronic Supplementary Information (ESI) available: [NMR and FT-IR spectra for **[W(CO)$_5$]-Bpy** (**1**), **[W(CO)$_5$]-(1PV-Py$_2$)** (**2**), and **[W(CO)$_5$]-(3PV-Py$_2$)** (**3**), additional figures for Molecular packings in **1-3** including a table describing the detail parameters including the occupancy of each atoms, and Disordered O, Si, and C atoms of OSi(*i*-Pr)$_3$ groups in [W(CO)$_5$]$_2$-(3PV-Py$_2$) (**3**), and CIF files for **1**, **2** and **3**, deposited as CCDC1409638-1409640]. See DOI: 10.1039/x0xx00000x

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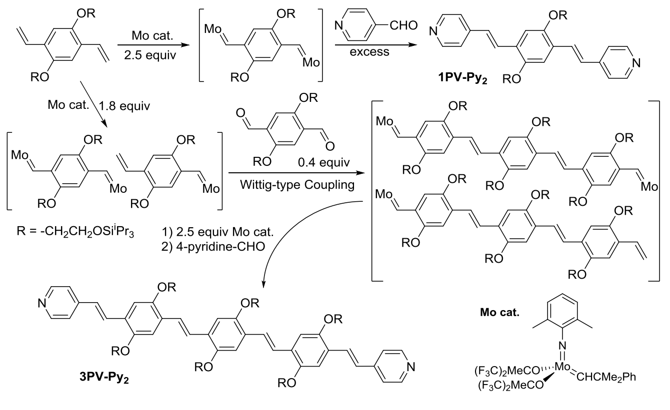
exclusive synthesis of a series of (substituted) OPV containing ligands at the both chain ends,[8] we thus explored a possibility for synthesis of metal dimers bridged with conjugated oligomers. We thus herein present synthesis and structural analysis of tungsten dimers bridged with OPV through pyridine ligands, and some basic optical properties. Through this study, we demonstrate a possibility for obtainment of structural information of these oligomers in a solid state (crystals).

Results and Discussion

1. Synthesis of tungsten-carbonyl dimers bridged by oligo(2,5-dialkoxy-1,4-phenylene vinylene)s by coordination of pyridine at the end groups, $[W(CO)_5]_2$-(nPV-Py_2).

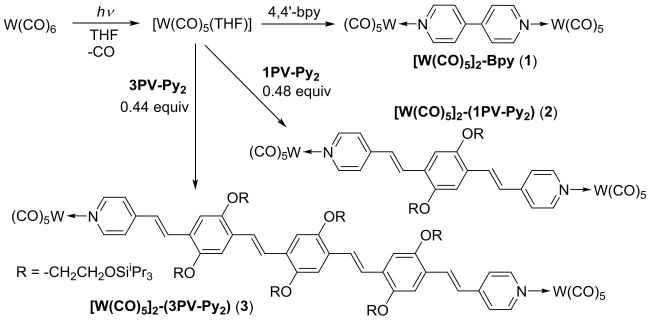
Two oligo(2,5-dialkoxy-1,4-phenylene vinylene)s (OPVs) containing pyridine as the end groups, expressed as ***n*PV-Py$_2$** [n = 1, 3; alkoxy = $O(CH_2)_2OSi^iPr_3$], have been prepared in high yields on the basis of our reported procedure[8] shown in Scheme 2. The vinyl groups in 2,5-bis(2'-triisopropylsilyloxyethoxy)-1,4-divinylbenzene (DVB) were treated with Mo(CHCMe$_2$Ph)-(N-2,6-Me$_2$C$_6$H$_3$)[OCCH$_3$(CF$_3$)$_2$]$_2$, (**Mo** cat., 2.5 equiv), to form the "bis-alkylidene" species *in situ*, and subsequent reaction with 4-pyridine carboxaldehyde (Py-CHO) in rather excess amount (10 equiv to DVB) afforded **1PV-Py$_2$** that was isolated by fractional separation (pouring the chloroform solution into cold methanol) and column chromatography. Moreover, DVB was treated with **Mo** cat. (1.8 equiv) in toluene and the mixture was then added to a toluene solution containing 0.4 equiv of 2,5-bis(2'-triisopropylsilyloxyethoxy)-benzene-1,4-dicarboxaldehyde, the mixture was then added **Mo** cat. for completion of the olefin metathesis and subsequent addition of excess Py-CHO afforded **3PV-Py$_2$** that was isolated by fractional separation including using column chromatography. These are an established methodology for synthesis of EF-OPVs with controlled repeat units,[8] and the resultant OPVs possessed strictly repeat units with well-defined end groups; the olefinic double bond possessed exclusively *trans* stereo-regularity (confirmed by ^{1}H NMR spectra, X-ray crystallography shown below), as reported previously.[8,16] These compounds were identified by NMR spectra, elemental analysis, and by (APCI) mass spectrometry, and their purities (without contamination of the other oligomers, polymers) were also confirmed by fractional GPC (in addition to ordinary GPC traces, M_w/M_n = 1.0).



Scheme 2. Synthesis of **1PV-Py$_2$** and **3PV-Py$_2$**.

It turned out as a preliminary model reaction that 4,4'-bipyridyl (bpy, 0.45 equiv to W) was treated with W(CO)$_5$(THF) prepared *in situ* from W(CO)$_6$ in THF under photo-irradiation using high pressure mercury lamp, affording the corresponding dimer, **[W(CO)$_5$]$_2$-Bpy (1)**, in moderate yield (72 %) that is higher than the reported procedure (prepared under dark conditions, required separation with unreacted products by extraction and column chromatography).[15a] Therefore, the resultant **1PV-Py$_2$** and **3PV-Py$_2$** were treated with W(CO)$_5$(THF) prepared *in situ* from W(CO)$_6$ to afford the corresponding tungsten-carbonyl dimers, **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** [n = 1 (**2**), 3 (**3**)], in moderate yields (62, 67 %, respectively, Scheme 3). These complexes were identified by NMR spectra, elemental analysis and their structures were determined by X-ray crystallography, shown below (Figures 1-3).[16]

Products **1-3** were also characterized by infrared spectroscopy analysis. FT-IR spectrum of **1** showed the carbonyl infrared stretching frequencies at about 2072, 1975, 1950, 1919, 1900, and 1869 cm^{-1}, which are similar to those previously reported for **1**.[15b] For **2** and **3** the four absorption bands were observed in carbonyl infrared stretching region, respectively (**2**: 2073, 1969, 1919, and 1865 cm^{-1}, **3**: 2070, 1969, 1927, and 1894 cm^{-1}). These bands are almost comparable to those of **1**, indicating that the W(CO)$_5$ moiety coordinated with the pyridine ligand exists in **2** and **3**.



Scheme 3. Synthesis of **[W(CO)$_5$]$_2$-Bpy** (**1**), and **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** [n = 1 (**2**), 3 (**3**)].

2. Structural analysis of $[W(CO_5)]_2$-Bpy, $[W(CO_5)]_2$-(1PV-Py_2), $[W(CO)_5]_2$-(3PV-Py_2).

Red microcrystals of **[W(CO)$_5$]$_2$-Bpy** (**1**), **[W(CO)$_5$]$_2$-(1PV-Py$_2$)** (**2**), and **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**) that are suitable for X-ray crystallographic analyses were grown from the CH$_2$Cl$_2$ solution layered by n-hexane. Their structures containing the selected bond distances and angles, and the torsion angles are shown in Figures 1-3, and crystal data and collection parameters are summarised below (Table 2, Experimental Section).[16] Although both of R$_1$ and wR$_2$ values of **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**) are rather higher than those of complexes **1** and **2**, due to the disordered Si^{i}Pr$_3$ groups (especially isopropyl groups),[16] X ray diffraction analysis of **1-3** reveals a 18 electron complex with a distorted octahedral geometry around the tungsten atom (Figures 1-3). The N-W-

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C(axial) and W-C(axial)-O angles in **1-3** are almost linear [**1**: 177.32(7), 178.60(18)º; **2**: 177.5(3), 178.9(8)º; **3**: 177.2(4), 176.6(10)º, respectively], and the W(1)-C bond distance for the axial CO ligand is shorter than those for the four equatorial CO ones of each complexes [**1**: axial 1.982(2) Å, equatorial 2.041(3)–2.058(2) Å; **2**: axial 1.946(10) Å, equatorial 2.015(11)–2.082(12) Å; **3**: axial 1.999(10) Å, equatorial 2.022(16)–2.066(12) Å]. The C-O bond distance for the axial CO is slightly longer than those for the four equatorial COs [**1**: axial 1.153(3) Å, equatorial 1.137(3)–1.144(3) Å; **2**: axial 1.194(12) Å, equatorial 1.127(15)–1.165(12) Å; **3**: axial 1.139(12) Å, equatorial 1.107(16)–1.16(2) Å]. These results suggest that dπ(W)-π*(CO) back donation is more effective for the axial CO than the equatorial COs, because of the σ-donation from the pyridyl moiety to W.

1PV-Py$_2$ and **3PV-Py$_2$** ligands in complexes **2**, **3** are reasonably assigned to the phenylene vinylene skeletons from the consideration of the C-C bond lengths and angles. The C-C double bonds of 3PV-Py$_2$ ligand are a little longer compared with that of 1PV-Py$_2$ **[3**: C(9)-C(10) 1.323(14), C(3)-C(4) 1.364(14) Å, **2**: C(3)-C(4) 1.313(13)**]**. The steric repulsions among triisopropylsilyloxyethoxy groups bonding to phenyl rings B and C exist in complex **3**, different to complex **2**. In addition, π-conjugation system can be expanded on **3PV-Py$_2$** ligand more than **1PV-Py$_2$** one. Thus, such the steric repulsion of triisopropylsilyloxyethoxy groups and/or the π-conjugation on the phenylene vinylene moiety may affect to these C-C bond lengths.

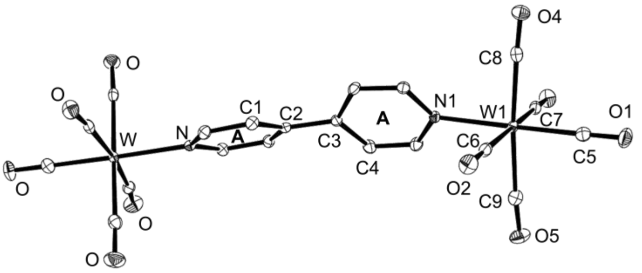

Figure 1. ORTEP drawings for **[W(CO)$_5$]$_2$-Bpy** (**1**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[16] Selected Bond Distances (Å): C(1)-C(2) 1.399(3), C(2)-C(3) 1.484(3), C(3)-C(4) 1.397(3), W(1)-N(1) 2.2683(17), W(1)-C(5) 1.982(2), W(1)-C(6) 2.055(2), W(1)-C(7) 2.041(2), W(1)-C(8) 2.042(2), W(1)-C(9) 2.058(2), C(5)-O(1) 1.153(3), C(6)-O(2) 1.140(3), C(7)-O(3) 1.144(3), C(8)-O(4) 1.144(3), C(9)-O(5) 1.137(3). Selected Bond Angles (º): N(1)-W(1)-C(5) 177.32(7), W(1)-C(5)-O(1) 178.60(18), N(1)-W(1)-C(6) 86.70(7), C(5)-W(1)-C(6) 91.19(8), C(6)-W(1)-C(8) 92.89(8), C(6)-W(1)-C(7) 176.54(8). Selected Torsion Angles (º): C(1)-C(2)-C(3)-C(4) 145.09(18).

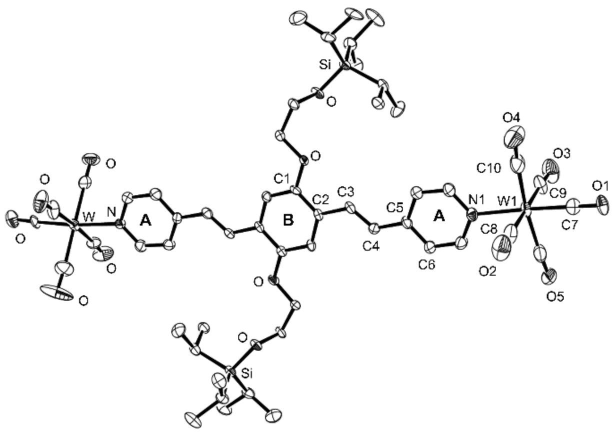

Figure 2. ORTEP drawings for **[W(CO)$_5$]$_2$-(1PV-Py$_2$)** (**2**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[16] Selected Bond Distances (Å): C(1)-C(2) 1.403(12), C(2)-C(3) 1.488(11), C(3)-C(4) 1.313(13), C(4)-C(5) 1.468(12), C(5)-C(6) 1.384(13), W(1)-N(1) 2.282(7), W(1)-C(7) 1.946(10), W(1)-C(8) 2.050(10), W(1)-C(9) 2.022(10), W(1)-C(10) 2.015(11), W(1)-C(11) 2.082(12), C(7)-O(1) 1.194(12), C(8)-O(2) 1.147(13), C(9)-O(3) 1.165(12), C(10)-O(4) 1.158(14), C(11)-O(5) 1.127(15). Selected Bond Angles (º): N(1)-W(1)-C(7) 177.5(3), W(1)-C(7)-O(1) 178.9(8), N(1)-W(1)-C(8) 87.0(3), C(7)-W(1)-C(8) 91.0(4), C(8)-W(1)-C(10) 90.7(5), C(8)-W(1)-C(9) 179.2(5). Selected Torsion Angles (º): C(1)-C(2)-C(3)-C(4) 177.2(7), C(3)-C(4)-C(5)-C(6) 179.3(7).

Two pyridyl rings (A) in **[W(CO)$_5$]$_2$-Bpy** (**1**) are twisted by 32.807° [C(1)-C(2)-C(3)-C(4) torsion angle is 145.09(18)°]. In contrast, the dihedral angle between A and B in **[W(CO)$_5$]$_2$-(1PV-Py$_2$)** (**2**) is 5.950°, and the C(1)-C(2)-C(3)-C(4) and C(3)-C(4)-C(5)-C(6) torsion angles of are 177.19° and 178.28°, respectively, that are close to 180°, clearly suggesting that the two pyridyl and centered phenyl rings (A, B) in **2** exist in the same plane. These structural features indicate that the π-conjugation system is extended on **1PV-Py$_2$** unit through an introduction of phenylene vinylene moiety between two pyridyl rings. However, the torsion angles of C(1)-C(2)-C(3)-C(4), C(3)-C(4)-C(5)-C(6), C(7)-C(8)-C(9)-C(10), and C(9)-C(10)-C(11)-C(12) in **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**) are smaller than those in **2** [177.2(7)-179.3(7)° in **2** *vs.* 158.2(8)-168.9(7)° in **3**], suggesting that both the pyridyl and the phenyl rings (A, B, C) in **3** are slightly twisted (the dihedral angle between A and B 34.261°, B and C 31.915°, respectively). As shown in Figure 4, there is an intermolecular interaction between the isopropyl group and the pyridyl ring (A) of another molecule in a crystal lattice, affecting that the ring (A) exists out of the plane of phenyl ring (B). It is thus assumed that a steric repulsion between Si^{i}Pr$_3$ and pyridyl groups may thus induce twisting the phenyl rings (B and C).

The molecular packings of the complexes **1**-**3** in the crystal unit cell (shown in ESI, Figure S2),[16] showed that **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**) molecules are arranged in parallel to each other in solid state, which is different from those in **[W(CO)$_5$]$_2$-Bpy** (**1**) and **[W(CO)$_5$]$_2$-(1PV-Py$_2$)** (**2**). Molecular size of **1**-**3** is 17.662, 26.904, 39.772 (39.612) Å, respectively. Complex **3** thus reveals the one-dimensional long molecular structure, may be possible to construct a parallel stack assembly. The distances between W atoms of complex **3** on the different layers are 12.054 and 11.691 Å, which are about three times shorter than the molecular size of **3**.

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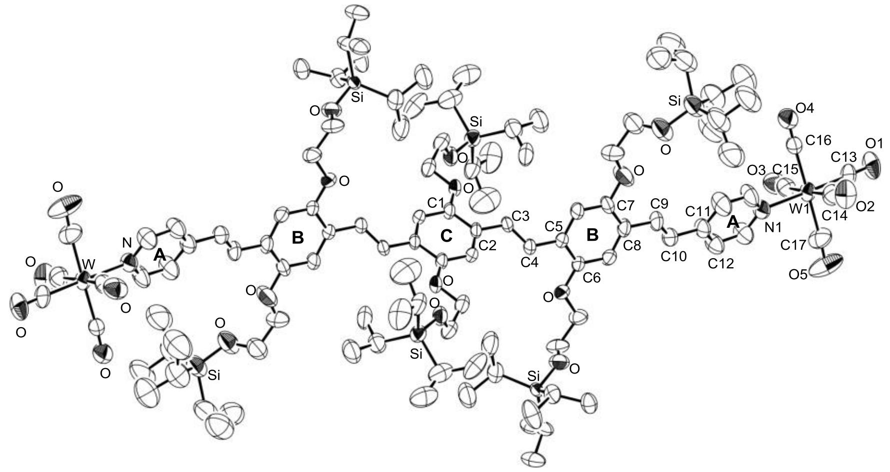

Figure 3. ORTEP drawings for **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**). Thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.[16] Selected Bond Distances (Å): C(1)-C(2) 1.400(14), C(2)-C(3) 1.484(10), C(3)-C(4) 1.364(14), C(4)-C(5) 1.472(10), C(5)-C(6) 1.438(14), C(7)-C(8) 1.427(15), C(8)-C(9) 1.452(10), C(9)-C(10) 1.323(14), C(10)-C(11) 1.477(10), C(11)-C(12) 1.379(13), W(1)-N(1) 2.278(6), W(1)-C(13) 1.999(10), W(1)-C(14) 2.066(12), W(1)-C(15) 2.045(12), W(1)-C(16) 2.022(16), W(1)-C(17) 2.051(15), C(13)-O(1) 1.139(12), C(14)-O(2) 1.107(16), C(15)-O(3) 1.122(15), C(16)-O(4) 1.16(2), C(17)-O(5) 1.11(2). Selected Bond Angles (º): N(1)-W(1)-C(13) 177.2(4), W(1)-C(13)-O(1) 176.6(10), N(1)-W(1)-C(14) 94.6(4), C(13)-W(1)-C(14) 87.4(4), C(14)-W(1)-C(16) 91.4(5), C(14)-W(1)-C(15) 169.5(4). Selected Torsion Angles (º): C(1)-C(2)-C(3)-C(4) 164.8(7), C(3)-C(4)-C(5)-C(6) 168.9(7), C(7)-C(8)-C(9)-C(10) 158.2(8), C(9)-C(10)-C(11)-C(12) 167.4(8).

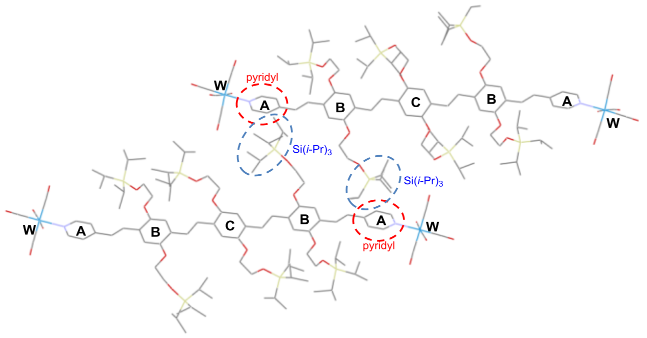

Figure 4. The interaction between the isopropyl and the pyridyl groups of **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**) in the crystal lattice. The colored circles indicate the isopropyl and the pyridyl groups, respectively.

3. UV-vis and fluorescence spectra for *n*PV-Py$_2$, and [W(CO)$_5$]$_2$-(*n*PV-Py$_2$) (n = 1,3).

Figure 5 shows UV-vis and fluorescence spectra of ***n*PV-Py$_2$**, and **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** [n = 1 (**2**), 3 (**3**), 1.0×10^{-6} M in THF at 25 ºC), and the λ_{max} values in the absorption, fluorescence and the quantum yields (Φ_{PL}) are summarised in Table 1. As reported previously, the absorption bands and the λ_{max} values ascribed to the lowest π-π* transition of the OPV backbone,[8,17] were shifted to longer wavelength (the maximum of the $S_1 \leftarrow S_0$ electronic transition shifts towards lower energies) upon increase in the conjugation units [**1PV-Py$_2$** and **3PV-Py$_2$**],[16] It should be noted that the λ_{max} values shifted to longer wavelength by coordination to tungsten, **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** [*n* = 1 (**2**), 2 (**3**)]. It has been reported that **[W(CO)$_5$]$_2$-Bpy** (**1**) shows two absorption bands ascribed to the ligand filed (^{1}E ← ^{1}A, 400 nm in Figure 5) and metal-to-ligand charge transfer (MLCT, π* ← ^{1}A, 425 nm in Figure 5).[15a] Moreover, the λ_{max} values ascribed to MLCT transfer became longer by placement of the bridge due to increasing the π conjugation, whereas the similar shift was not observed in the mononuclear species, [W(CO)$_5$]-Bpy.[15a] Therefore, we can at least say that the shift of the λ_{max} values in **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** [*n* = 1 (**2**), 2 (**3**)] would be ascribed to dimeric structures through ***n*PV-Py$_2$** in these complexes.

As also reported previously, the recorded fluorescence spectra showed a vibronic splitting where the relative intensity of the $S_1 \rightarrow S_0$ 0–0 compared to the 0–1 electronic transition seems to increase upon increasing the π conjugation length;[8,17b,18] because the λ_{max} values increased in the order: 457 and 473 nm (**1PV-Py$_2$**) < 506 nm (**2**) < 519 (**3PV-Py$_2$**) < 559 nm (**3**). Note that redshift of the λ_{max} value with significant decrease in the photoluminescence quantum yields (Φ_{PL}) was observed by coordination of ***n*PV-Py$_2$** to tungsten.[8b,10e,f,19] Degree of the decrease (quenching) was affected by the conjugation length as reported previously.[10e,f] On the basis of both UV-vis and fluorescence spectra, it is suggested that these λ_{max} values in these π conjugated molecules were affected by expansion of the conjugation by coordination of tungsten as well as of push/pull character of the chromophore.

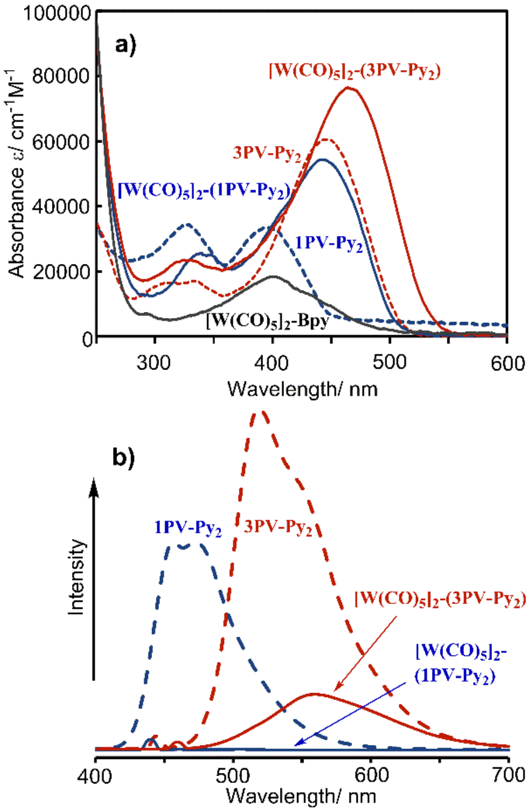

Figure 5. UV-Vis (top) and fluorescence (bottom) spectra of ***n*PV-Py$_2$**, and **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** (n = 1,3; 1.0×10^{-6} M in THF at 25 ºC).

Concluding Remarks

We have prepared tungsten carbonyl dimers bridged with oligo(2,5-dialkoxy-1,4-phenylene vinylene)s (OPV) through coordination with pyridine as the end groups, expressed as **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** [*n* = 1 (**2**), 3 (**3**); alkoxy = O(CH$_2$)$_2$OSi^{i}Pr$_3$], from W(CO)$_6$ with ***n*PV-Py$_2$** in THF under photoirradiation, and their structures were determined by X ray crystallography. It turned out that the π-conjugation system is extended on **1PV-Py$_2$** unit through an introduction of phenylene vinylene moiety between two pyridyl rings, whereas the torsion angles in **[W(CO)$_5$]$_2$-(3PV-Py$_2$)** (**3**) are rather smaller than those in **2**, probably due to an intermolecular interaction between the isopropyl group and the pyridine moiety in the lattice of **3**. Both increase in the absorbance intensity and redshift in the λ_{max} values in **[W(CO)$_5$]$_2$-(*n*PV-Py$_2$)** from their ***n*PV-Py$_2$** in UV-vis spectra were observed owing to increase in conjugation length through coordination to W metal center. As described in the introductory, not only examples for synthesis of a series of well-defined, end-functionalized OPVs (EF-OPVs), but also, in particular, structural analysis of the oligomer by isolation as transition metal complexes have been limited so far. Therefore, we believe the approach introduced here would be helpful for better design and basic understanding of precise conjugated materials for the desired purposes.

Table 1. Summary of optical properties of 1PV-Py$_2$, [W(CO)$_5$]$_2$-(1PV-Py$_2$) (2), 3PV-Py$_2$ and [W(CO)$_5$]$_2$-(3PV-Py$_2$) (3).

	$M_{n(calcd)}$[a]	absorption[b] λ_{max}/ nm (ε /10^5 cm^{-1}M^{-1})	fluorescence[c] λ_{max}/ nm	Φ_{PL}[d]
1PV-Py$_2$	717	326 (0.34), 396 (0.33)	457, 473	0.592
W(CO)$_5$]$_2$-(1PV-Py$_2$) (2)	1365	340 (0.26), 441 (0.54)	506	0.007
3PV-Py$_2$	1787	333 (0.17), 446 (0.60)	519	0.556
W(CO)$_5$]$_2$-(3PV-Py$_2$) (3)	2435	324 (0.23), 464 (0.76)	559	0.136

[a]Calculated on the basis of formula, molar ratios. [b]By UV-vis spectra (in THF conc. 1.0×10^{-6} M at 25 ºC). [c]By fluorescence spectra (in THF conc. 1.0×10^{-6} M at 25 ºC), excitation at 390 nm (**1PV-Py$_2$**), 400 nm for **[W(CO)$_5$]$_2$-Bpy**, 440 nm for **[W(CO)$_5$]$_2$-(1PV-Py$_2$)**, for 445 nm **3PV-Py$_2$**, 460 for **[W(CO)$_5$]$_2$-(3PV-Py$_2$)**, respectively. [d]Photoluminescence quantum yield (in THF conc. 1.0×10^{-6} M at 25 ºC), at excitation wavelength (described above, λ_{max} in their UV-vis).

Experimental Section

General procedure.

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All chemicals used were of reagent grades and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox, and was stored over sodium/potassium alloy in the drybox, and then passed through an alumina short column prior to use. Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)[OCMe(CF$_3$)$_2$]$_2$ (**Mo** cat.)[20] was prepared according to the literature. 4-Pyridinecarboxaldehyde (Tokyo Chemical Industry Co.), W(CO)$_6$ (Sigma-Aldrich Co.), 4,4′-bipyridyl (Kanto Chemical Co., Inc.) were used as received without further purification. Synthesis of 2,5-bis(2'-triisopropyl-silyloxyethoxy)-1,4-divinylbenzene (DVB) and 2,5-bis(2'-triisopropylsilyloxyethoxy)benzene-1,4-dicarboxaldehyde were prepared according to our previous manuscript.[8a] Elemental analyses were performed by using EAI CE-440 CHN/O/S Elemental Analyzer (Exeter Analytical, Inc.). All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer (399.8 MHz for ^{1}H, 100.5 MHz for ^{13}C) and all chemical shifts are given in ppm and are referenced to SiMe$_4$. Obvious multiplicities and routine coupling constants are usually not listed, and all NMR spectra were obtained in the solvent indicated at 25 ºC unless otherwise noted. Atmospheric pressure chemical ionization (APCI) mass spectrometry was obtained on Burker MicrOTOF II-SDT1. Preparative gel-permeation chromatography (GPC) was performed on a YMC LC-Forte/R (YMC group) using UV detector in toluene with flow rate 10.0 mL/min, equipped with YMC-GPC T4000 and YMC-GPC T30000 columns, ranging

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from 4×10^3 to 30×10^3 MW. Infrared spectra were recorded on SHIMADZU IRAffinity-1 Fourier transform infrared spectrophotometer. UV-vis spectra for the resultant oligomers were measured by using a Jasco V-550 UV/vis spectrophotometer (conc. 1.0×10^{-6} M in THF at 25 ºC), and the fluorescence spectra were measured by Hitachi F-4500 fluorescence spectrophotometer (under absorbance 0.1 in THF at 25 ºC) with the λmax values in the UV-vis spectra (shown in the Figure caption). Fluorescence quantum yields were measured by Hamamatsu photonics C9920-02G (ex. under absorbance at 0.1 in THF at 25 ºC).

Synthesis of 1PV-Py$_2$.

In the drybox, a toluene solution (2.0 mL, 8.9 mM) containing 2,5-bis(2'-triisopropylsilyloxyethoxy)-1,4-divinylbenzene (DVB, 10 mg, 17.8 µmol) was added a toluene solution (1.0 mL) containing Mo(CHCMe$_2$Ph)(N-2,6-Me$_2$C$_6$H$_3$)-[OCMe(CF$_3$)$_2$]$_2$ (**Mo** cat., 32 mg, 44.4 µmol, 2.5 equiv), and the mixture was stirred at room temperature for 2 h. The reaction mixture was then added 4-pyridinecarboxaldehyde (PyCHO) in excess amount (19.0 mg, 177.4 µmol) (10 equiv. to DVB), and the mixture was stirred for an additional 1 h for completion. The reaction mixture was poured into a cold 10 mM HCl aqueous solution (10 mL), and the mixture was stirred for 2 h. The organic products were extracted with chloroform. The chloroform solution was filtered through a Celite pad, the filtercake was washed with chloroform (100 mL). The combined organic layer was further washed with a saturated aqueous K_2CO_3 solution twice. The organic layer was then dried over anhydrous $MgSO_4$, and was placed in a rotary evaporator to remove volatiles. The resultant oil was purified by simple fractional separation (for obtainment of **1PV-Py$_2$** as precipitates of pouring the concentrated chloroform solution into cold methanol) and a silica gel column chromatography (100% chloroform), affording yellow solids. Yield 10.5 mg (83 %). ^{1}H NMR (CDCl$_3$ at 25 ºC): δ 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). ^{13}C NMR (CDCl$_3$ at 25 ºC): δ 151.5, 149.3, 145.7, 131.0, 128.3, 127.0, 126.4, 110.8, 71.0, 62.3, 18.0, 12.0. APCI-MS calcd for $C_{42}H_{64}N_2O_4Si_2$ = 717.15, found *m/z* = 716. Anal. Calcd. for $C_{42}H_{64}N_2O_4Si_2$: C, 70.34; H, 9.00; N, 3.91. Found: C 70.40; H, 8.93; N, 3.74. $M_{\mathrm{n(calcd)}}$ = 717, $M_{\mathrm{n(NMR)}}$ = 720.

Synthesis of 3PV-Py$_2$.

A toluene solution (2.0 mL, 8.9 mM) containing DVB (10 mg, 17.8 µmol) was added a toluene solution (1.0 mL) containing **Mo** cat. (23 mg, 31.9 µmol, 1.8 equiv), and the mixture was stirred at room temperature for 2 h. The solution was then added to a toluene solution (0.5 mL) containing 2,5-bis(2'-triisopropyl-silyloxyethoxy)benzene-1,4-dicarboxaldehyde (4.0 mg, 7.06 µmol, 0.4 equiv to DVB) and stirred for 1 h. The reaction mixture was then added to a toluene solution (1.0 mL) containing **Mo** cat. (32 mg, 44.4 µmol, 2.5 equiv to DVB) at room temperature, and the reaction mixture was stirred for 1 h for completion of the reaction with the vinyl group. The reaction mixture was then treated by addition of PyCHO in excess amount (10 equiv. to the DVB), and the mixture was stirred for an additional 1 h to provide the 3 mers (**3PV-Py$_2$**). The mixture was poured into a cold 10 mM HCl aqueous solution (10 mL), and the mixture was stirred for 2 h.. The organic products were extracted with chloroform (100 mL). The chloroform solution was filtered through a Celite pad, the filtercake was washed with chloroform. The combined organic layer was further washed with a saturated aqueous K_2CO_3 solution twice. The organic layer was then dried over anhydrous $MgSO_4$, and was placed in a rotary evaporator to remove volatiles. The resultant oil was purified by simple fractional separation (pouring the concentrated chloroform solution into cold methanol, isolated as precipitates) and a silica gel column chromatography (100% chloroform), affording orange solids. Yield 8.9 mg (71 %). ^{1}H NMR (CDCl$_3$ at 25 ºC): δ 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). ^{13}C NMR (CDCl$_3$ at 25 ºC) : δ 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. APCI-MS calcd for $C_{102}H_{172}N_2O_{12}Si_6$ = 1787.01, found *m/z* = 1786. Anal. Calcd. for $C_{102}H_{172}N_2O_{12}Si_6$: C, 68.56; H, 9.70; N, 1.57. Found: C 68.45; H, 9.92; N, 1.41. $M_{\mathrm{n(calcd)}}$ = 1787, $M_{\mathrm{n(NMR)}}$ = 1798.

Synthesis of [W(CO)$_5$]$_2$-Bpy (1).

In the drybox, W(CO)$_6$ (30.0 mg, 85.2 µmol) and tetrahydrofuran (10 mL) were mixed into a sealed Schlenk-tube. The solution was irradiated under UV light using ultra high pressure mercury lamp at room temperature for 5 h. The color of solution rapidly changed from colorless to strong yellow, suggesting generation of W(CO)$_5$(THF) *in situ*. Into the reaction mixture containing W(CO)$_5$(THF), a THF solution (2.0 mL) containing 4,4′-bipyridyl (6.0 mg, 38.4 µmol, $\leq$0.45 equiv) was added, and the solution was stirred overnight. The color of the reaction mixture changed gradually from yellow to orange-red. The solution was then placed *in vacuo* to remove volatiles. The resultant solids were dissolved with toluene, and the solution was passed through a Celite pad and the filtercake was further washed with toluene. The combined solution was concentrated *in vacuo*, and the resultant solids were recrystallized with dichloromethane layered by *n*-hexane (1:3, v/v) at -30 ˚C. The chilled solution gave yellow microcrystals. Yield 22.1 mg (72 %). The present synthetic procedure for **1** is different from that reported previously (under dark conditions),[15a] and afforded **1** in rather high yield. ^{1}H NMR (CDCl$_3$ at 25 ºC): δ 9.02 (d, 4H), 7.49 (d, 4H). ^{13}C NMR (CDCl$_3$ at 25 ºC): δ 198.6, 157.1, 122.8. IR (KBr) (cm^{-1}): 2072 (m) ν_{CO}, 1975 (w) ν_{CO}, 1950 (w) ν_{CO}, 1919 (s) ν_{CO}, 1900 (s) ν_{CO}, 1869 (s) ν_{CO}. Anal.Calcd for $C_{20}H_8N_2O_{10}W_2$: C, 29.88; H, 1.00; N, 3.48. Found: C 30.17; H, 1.09; N, 3.51.

Synthesis of [W(CO)$_5$]$_2$-(1PV-Py$_2$) (2).

Synthetic procedure for **[W(CO)$_5$]$_2$-(1PV-Py$_2$)** (**1**) is similar to that in **1**, except that W(CO)$_6$ (20.0 mg, 56.8 µmol), **1PV-Py$_2$** (18.0 mg, 25.1 µmol, 0.48 equiv) in place of 4,4′-

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bipyridyl were used. The color of the reaction mixture changed gradually from yellow to orange-red. The solution was then placed *in vacuo* to remove volatiles. The resultant solids were dissolved with toluene, and the solution was passed through a Celite pad and the filtercake was further washed with toluene. The combined solution was concentrated *in vacuo*, and the resultant solids were recrystallized with dichloromethane layered by *n*-hexane (1:3, v/v) at -30 ˚C. The chilled solution gave orange microcrystals. Yield 23.2 mg (67.7%). ^{1}H NMR ($CDCl_3$ at 25 ºC): δ 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). ^{13}C NMR ($CDCl_3$ at 25 ºC): δ 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. IR (KBr) (cm^{-1}): 2073 (m) ν_{CO}, 1969 (w) ν_{CO}, 1919 (s, br) ν_{CO}, 1865 (s) ν_{CO}. Anal. Calcd. for $C_{52}H_{64}N_2O_{14}Si_2W_2$: C, 45.76; H, 4.73; N, 2.05. Found: C 45.87; H, 4.75; N, 1.97.

Synthesis of $[W(CO)_5]_2$-(3PV-Py_2) (3).

Synthetic procedure for **$[W(CO)_5]_2$-(3PV-Py_2)** (**3**) is similar to that in **1**, except that $W(CO)_6$ (8.0 mg, 22.7 μmol), **3PV-Py_2** (18.0 mg, 10.1 μmol, 0.44 equiv) in place of 4,4′-bipyridyl were used. The colour of the reaction mixture changed gradually from yellow to orange-red. The solution was then placed *in vacuo* to remove volatiles. The resultant solids were dissolved with toluene, and the solution was passed through a Celite pad and the filtercake was further washed with toluene. The combined solution was concentrated *in vacuo*, and the resultant solids were recrystallized with dichloromethane layered by *n*-hexane (1:3, v/v) at -30 ˚C. The chilled solution gave red microcrystals. Yield 15.2 mg (62.0 %). ^{1}H NMR ($CDCl_3$ at 25 ºC): δ 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). ^{13}C NMR ($CDCl_3$ at 25 ºC): δ 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. IR (KBr) (cm^{-1}): 2070 (m) ν_{CO}, 1969 (w) ν_{CO}, 1927 (s, br) ν_{CO}, 1894 (s) ν_{CO}. Anal. Calcd for $C_{112}H_{172}N_2O_{22}Si_6W_2$: C, 55.25; H, 7.12; N, 1.15. Found (1): C 54.84; H, 7.14; N, 1.05. Found (2): C 54.79; H, 7.17; N, 1.05. C value seems somewhat low probably due to incomplete combustion (formation of WC partially), and the analysis results were reproducible.

Crystallographic analysis.

All measurements were made on a Rigaku Micro Max-007HF Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation. The selected crystal collection parameters are listed in Table 2, and the detailed results were described in the reports in the Electronic Supplementary Information (ESI). All structures were solved by direct methods.[21] and expanded using Fourier techniques, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the Crystal Structure[22] crystallographic software package except for refinement, which was performed using SHELXL-97.[23] Detailed analysis data including the collection parameters, CIF files, and the structure reports are shown in the Electronic Supplementary Information (ESI).[16] X Ray diffraction analysis of **1-3** reveals a 18 electron complex with a distorted octahedral geometry around the tungsten atom (Figures 1-3). The pyridyl groups of both sides of Bpy, 1PV-Py_2, and 3PV-Py_2 coordinate to the axial position of the $W(CO)_5$ moiety. CCDC reference numbers for **$[W(CO)_5]_2$-Bpy** (**1**), **$[W(CO)_5]_2$-(1PV-Py_2)** (**2**), and **$[W(CO)_5]_2$-(3PV-Py_2)** (**3**) are CCDC1409638-1409640, respectively.

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Table 2. Crystal data and collection parameters of **$[W(CO)_5]_2$-Bpy** (**1**), **$[W(CO)_5]_2$-(1PV-Py_2)** (**2**), **$[W(CO)_5]_2$-(3PV-Py_2)** (**3**).[a]

	$[W(CO)_5]_2$-Bpy (1)	**$[W(CO)_5]_2$-(1PV-Py_2) (2)**	**$[W(CO)_5]_2$-(3PV-Py_2) (3)**
Formula	$C_{20}H_8N_2O_{10}W_2$	$C_{52}H_{64}N_2O_{14}Si_2W_2$	$C_{224}H_{344}N_4O_{44}Si_{12}W_4$
Formula weight	803.99	1364.95	4869.61
Crystal color, habit	red, prism	orange, chip	red, prism
Crystal size (mm)	0.340×0.170×0.140	0.620×0.320×0.100	0.320×0.270×0.030
Crystal system	orthorhombic	monoclinic	triclinic
Space group	Pbca (#61)	$P2_1$ (#4)	P-1 (#2)
a (Å)	22.658(2)	7.7881(14)	15.2723(10)
b (Å)	14.6316(16)	28.597(5)	17.9800(13)
c (Å)	13.4069(14)	13.292(2)	23.720(2)
α (deg)			79.707(5)
β (deg)		101.790(5)	83.506(6)
γ (deg)			74.287(5)
V (Å^3)	4444.7(8)	2897.9(8)	6154.7(8)
Z value	8	2	1
D_{calcd} (g/cm^3)	2.403	1.564	1.314
F_{000}	2960.00	1356.00	2532.00
Temp (K)	93	93	93
μ (MoKα) (cm^{-1})	104.153	40.731	19.911
No. of reflections measured	136137	53693	112852
$2\theta_{max}$ (deg)	55.0	55.1	55.1
No. of observations [I > 2.00σ(I)]	5073	12785	28253
No. of variables	307	649	1679
R1 [I > 2.00σ(I)]	0.0120	0.0364	0.0893
wR2 [I > 2.00σ(I)]	0.0292	0.0836	0.2643
Goodness of Fit	1.143	1.004	1.086

[a] CIF files are shown in the Electronic Supplementary Information (ESI), and data are deposited as CCDC1409638-1409640.

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16 NMR and FT-IR spectra of these complexes are shown in the Electronic Supplementary Information (ESI). CIF files for **$[W(CO)_5]_2$-Bpy** (**1**), **$[W(CO)_5]_2$-(1PV-Py_2)** (**2**), and **$[W(CO)_5]_2$-(3PV-Py_2)** (**3**) are also shown in the ESI. The data for **1-3** are deposited as CCDC1409638-1409640. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/pages/Home.aspx In the structural analysis of **$[W(CO)_5]_2$-(3PV-Py_2)** (**3**), some isopropyl groups possess disorders even after refinement [R_1 = 0.0893; wR_2 = 0.2643; GOF = 1.086]. Figures for 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 are shown in the ESI.

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Contents Abstract

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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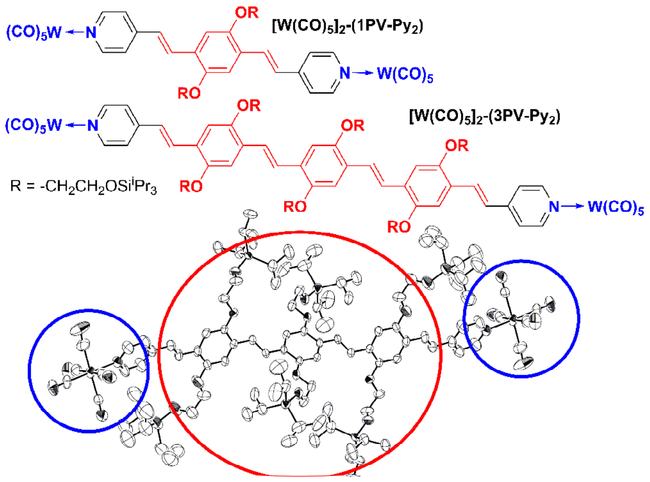
Synthesis, structural analysis and basic optical properties of tungsten carbonyl dimers bridged with oligo(2,5-dialkoxy-1,4-phenylene vinylene)s through coordination with pyridine have been explored.



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