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From Mesomorphic Phosphine Oxide to Clustomesogens Containing Molybdenum and Tungsten Octahedral Cluster Cores[**]

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Abstract: *New clustomesogens (i.e., metal atom clusters containing liquid crystalline (LC) materials) have been obtained by grafting neutral cyanobiphenyl (CB)- or cholesteryl-containing tailor-made dendritic mesomorphic triphenylphosphine oxide ligands on luminescent* $(M_6Cl^i_8)^{4+}$ *octahedral cluster cores (M = Mo, W). The LC properties were studied by a combination of polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray powder diffraction analyses. While the organic ligands showed various mesophase types ranging from nematic, SmA columnar* (SmA_{Col})*, SmA, and SmC phases, it turned out that the corresponding clustomesogens formed layered phases (SmA) over a wide range of temperatures that depend on the nature and density of mesogenic groups employed. Intrinsic luminescence properties of the cluster precursors are preserved over the entire range of LC phase existence.*

Liquid crystals are self-assembling molecular materials that have found various applications ranging from the manufacturing of liquid crystal display (LCD) to different molecular sensors and detectors, optical switches, spatial light modulator, etc., based on their unique features to retain a high degree of mobility besides long or short-range ordering in the fluid phase that give rise to anisotropy-related optical, electrical, and magnetic properties.[1] On the other hand, metal atom clusters are versatile building blocks for the design of hybrid nanomaterials with potential applications, for instance, in the fields of lighting, displays, and biolabeling technologies.[2] Association of organic mesogenic moieties with octahedral metallic cluster complexes led to a new family of liquid crystals, namely the clustomesogens, which exhibit interesting photoluminescence properties in the red-near-infrared region due to the cluster core.[3] In the light of recent findings, quantum yields of nanometer-sized octahedral clusters can reach values above 60%.[4] The affordable costs and preparation methods as well as thermal stability, the ease of handling and processing make them very appealing materials to be used in different applications based on emission properties (LED, lighting displays, etc.). Combining such nanoobjects with liquid-crystalline ordering is a challenging task[5] and so far, several strategies based on covalent binding or ionic self-assembly (ISA) were successfully employed to induce liquid crystalline (LC) properties in systems containing bulky entities, such as fullerene[6] and polyoxometalates.[7,8] On the other hand, phosphine or phosphine oxide ligands were scarcely used in the design of liquid-crystalline materials, mainly due to their inappropriate geometry concerning the molecular requirements to generate mesomorphic behavior.[9] Moreover, even if they are widely used as ligands in coordination chemistry only few examples of phosphine-oxide-containing metallomesogens (metal-containing liquid crystals) are known.[10] Generally, only less bulky phosphines, such as trialkylphosphine (alkyl = methyl, ethyl, propyl), were employed as co-ligands besides the other mesogenic ligands. Recently, it has been shown that the triphenylphosphine oxide core can be successfully used as a scaffold to obtain columnar liquid crystals that can interact easily with alkali metals to allow a switch between columnar and cubic phases.[11] In this Communication, we show that cholesteryl- and cyanobiphenyl-based phosphine oxide ligands constitute a valuable class of compounds that can be successfully used to design LC hybrid materials and in particular clustomesogens. By using long flexible alkyl chains to link the mesogenic groups to the coordinating unit, we prove that it is possible to decouple the mesogenic entities motion from the bulky metallic $(M_6Cl^i_8)^{4+}$ cluster core within the $[(M_6Cl^i_8)L^a_6]^{4+}$ building blocks, further abbreviated as $\mathbf{ML^{1-4}}$ (M = Mo and W). This strategy is related to the one used to incorporate a functional moiety in LC-dendrimers[12] or the preparation of LC hybrid systems made of inorganic nanoparticles[13] as well as the design of metallomesogens with high coordination numbers.[14] Hence, resulting clustomesogens display typical layered LC phases with transition temperatures influenced by the type and number of mesogenic groups grafted in the apical position of the $(M_6Cl^i_8)^{4+}$ octahedral cluster core while the emissive properties of the latter are kept almost unchanged. By using different neutral

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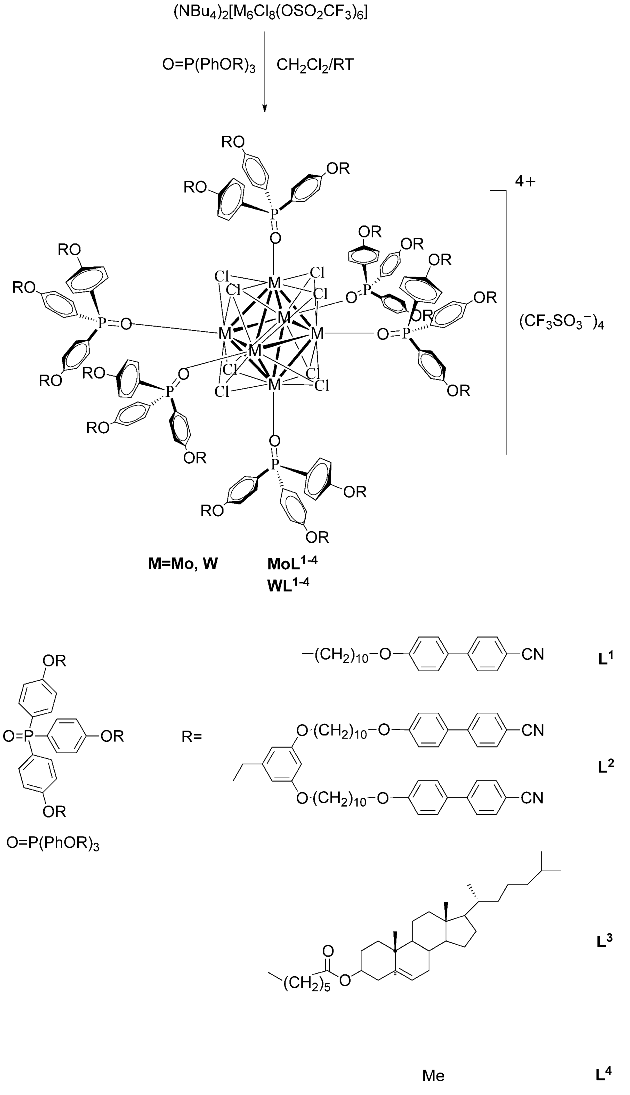
phosphine oxide ligands, we modified the mesogenic density surrounding the rigid metallic scaffold, which allows a deeper understanding of the requirements to control the nanostructuration and self-assembling abilities of these supermolecular systems in order to be able to adjust at will their self-organization according to targeted applications. The grafting of six neutral ligands onto the octahedral metallic clusters was initially investigated by using the tris(*p*-methoxyphenyl)phosphine oxide, the intermediate organic ligand without mesogenic groups, starting from hexa-triflate $[M_6Cl^i_8(CF_3SO_3)_6]^{2-}$ (M = Mo, W) precursors. Resulting $(CF_3SO_3)_4[M_6Cl^i_8(O{=}P(PhOMe)_3)^a_6]$ with M = Mo or W for compounds **MoL^4** and **WL^4**, respectively, were isolated as yellow crystals that were subjected to single-crystal X-ray diffraction studies confirming the formation of Mo_6 and W_6 hexa-functionalized metallic clusters with formation of a M−O bond between the $(M_6Cl^i_8)^{4+}$ cluster core and organic ligand (see the Supporting Information (SI) for crystallographic details).



Scheme 1. Preparation of new hexa-functionalized Mo_6 and W_6 clusters.

The ^{31}P NMR solution spectra of functionalized Mo_6 and W_6 clusters showed not only one signal, but a multiplet around 55 ppm assigned to the coordinated ligands, together with a very weak and broad signal around 30 ppm assigned to the free ligand. This is in stark contrast to the previously reported NMR data for hexa-substituted Mo_6 and W_6 clusters with triphenylphosphine ligands for which only one signal in the ^{31}P NMR spectrum was recorded.[15] This information could be interpreted by the existence of two competing factors: the non-equivalence of the six apical ligands due to structural conformation and a possible exchange between apical ligands and outer counteranions in solution. These findings determined us to have a closer look at the X-ray crystal structure of compounds **MoL^4** and **WL^4** revealing that the six M−O bonds are not equivalent (Table S2 in SI). Further, the monitoring by ^{31}P NMR spectroscopy of the addition of an excess of phosphine oxide **L^4** to the solution of **MoL^4** led to the collapse of the multiplet signal into two singlets and to the increase of the free ligand signal intensity thus evidencing the ligand exchange (Figure S13). Moreover, temperature-dependent ^{31}P NMR spectroscopy experiments realized with a CD_2Cl_2 solution of **MoL^4** showed upon cooling the disappearance of this last signal together with a clear narrowing of the multiplet corresponding to the grafted ligands (Figure S14). The mesogenic phosphine oxides **L$^{1-3}$** were prepared in moderate to good yield in a straightforward manner by the reaction of tris(4-hydroxyphenyl)phosphine oxide with corresponding bromide derivatives.[11,16] The covalent hexa-functionalization of the Mo_6 and W_6 metallic clusters has been achieved by a ligand-exchange reaction between the $[M_6Cl_8(CF_3SO_3)_6]^{2-}$ cluster unit with a slight excess of mesogenic phosphine oxide ligand in dichloromethane at room temperature (Scheme 1).[15] The purity of all compounds was assessed by elemental analysis. The IR spectra of hexa-substituted Mo_6 and W_6 clusters show several shoulders in the 1100–1200 cm^{-1} range assigned to the $CF_3SO_3^-$ ion together with a medium intensity absorption band in the 1000–1100 cm^{-1} range due to P=O vibration (Figures S19–S22). The ^{31}P NMR spectra contain the same features as those found for non-mesogenic Mo_6 and W_6 clusters **MoL^4** and **WL^4**, for example, a multiplet around 55 ppm and a broad signal centered around 30 ppm, suggesting a similar behavior in solution with six apical ligands around the cluster unit (Figure S8). The LC phases exhibited by both organic ligands and their respective clustomesogens were assigned based on the polarized optical microscopy (POM) textures as well as by variable-temperature powder X-ray diffraction and differential scanning calorimetry (DSC) studies. Their transition temperatures and the liquid crystalline properties are collected in Table 1. Whereas mesogenic organic ligand **L^1** shows typical textures for a nematic phase, the mesogenic phosphine oxide **L^2** shows a pseudo-focal conic texture that was assigned to a lamellar columnar phase (SmA_{Col}).[14] The POM pictures are shown in Figures S45–S52. Interestingly, the X-ray diffractogram of **L^2** shows two strong reflections in the small-angle region in the 1:2 ratio that correspond to a periodicity of 45.3 Å due to a multilayered smectic phase formed by the piling of triphenyloxide- and cyanobiphenyl-containing sublayers alternating with the aliphatic spacer sublayer. The abnormal intensities profile in the

Table 1: Transition temperatures, mesophase assignment, and interlayer distances for compounds $\mathbf{MoL^{1-3}}$ and $\mathbf{WL^{1-3}}$.

Cmpd	Transition[a]	T [°C][b]	ΔH [kJ mol^{-1}]	ΔH per mesogenic unit/[kJ mol^{-1}]	d [Å] (T [°C])
$\mathbf{L^1}$	g–N	15	–	–	
	N–I	32	–[c]	–	
$\mathbf{L^2}$	g–SmA$_{Col}$	24	–	–	45.3
	SmA$_{Col}$–I	69	21.7	3.6	(65)
$\mathbf{L^3}$	g–SmC	54	–	–	49.5
	SmC–SmA	95	–[d]	–	(70)
	SmA–I	137	9.3	3.1	
$\mathbf{MoL^1}$	g–SmA	33	–	–	35.7
	SmA–I	47	5.0	0.3	(40)
$\mathbf{WL^1}$	g–SmA	32	–	–	35.9
	SmA–I	50	–[c]	–	(40)
$\mathbf{MoL^2}$	g–SmA	33	–	–	42.5
	SmA–I	87	75.6	2.1	(80)
$\mathbf{WL^2}$	g–SmA	39	–	–	42.8
	SmA–I	94	102.6	2.9	(80)
$\mathbf{MoL^3}$	g–SmA	50	–	–	50.5
	SmA–I (dec.)	166	44.6	2.5	(160)
$\mathbf{WL^3}$	g–SmA	54	–	–	51.0
	SmA–I (dec.)	174	53.7	3.0	(170)

[a] g = glass, N = nematic, SmA$_{Col}$ = lamellar-columnar, SmA = smectic A, I = isotropic phase. [b] Temperatures are given as the onset values recorded in the second heating run, except compounds $\mathbf{MoL^3}$ and $\mathbf{WL^3}$; glass temperatures were recorded in the second cooling run as the inflexion point; [c] transition not detected by DSC; temperature was assigned by POM; [d] $\Delta Cp = 0.1$ kJ mol^{-1} K^{-1}.

diffractogram of $\mathbf{L^2}$ (Figure S24) with an intense d_{002} reflection compared to the d_{001} reflection was already found for typical bilayered smectic phases due to a pronounced segregation at the molecular level, between different units, for example, cyanobiphenyl units, aliphatic spacers, and the triphenylphosphine core.[17] Another broad reflection was seen around 13.2 Å and was assigned to some lateral periodicity within the layer due to the triphenylphosphine oxide units that show a strong tendency to stack into columns as previously shown by Kato and Hatano.[11] The cholesteryl-based organic ligand $\mathbf{L^3}$ displays two enantiotropic layered phases with a slight decrease of interlayer distance on decreasing the temperature below 95 °C (Figure S25) assigned to SmA and SmC phases. The latter phase was also evidenced by the typical Schlieren texture developed in the homeotropic regions of the previous SmA phase. The tilt angle was estimated to 18° at 60 °C from SAXS data.

Although clustomesogens $\mathbf{MoL^1}$ and $\mathbf{WL^1}$, possessing 18 cyanobiphenyl mesogenic groups around the cluster core, show an enantiotropic SmA phase at relatively low temperatures, the clustomesogens $\mathbf{MoL^3}$ and $\mathbf{WL^3}$ with bulkier cholesteryl-based mesogenic groups show an extended stability range of SmA phase (166 °C for $\mathbf{MoL^3}$ and 174 °C for $\mathbf{WL^3}$) up to the clearing point when decomposition occurs. On the other hand, the hexa-substituted clusters with 36 cyanobiphenyl mesogenic groups, $\mathbf{MoL^2}$ and $\mathbf{WL^2}$, show both only one very sharp enantiotropic transition from isotropic liquid to the mesophase and no sign of thermal decomposition after reaching the isotropic phase (Figures S41 and S42). On subsequent heating–cooling cycles, the DSC traces were reproducible and the transition temperatures did not change. All samples show a glass transition on heating or cooling and no sign of crystallization. Obviously, the transition temperatures depend significantly on the number and type of mesogenic units per cluster unit employed as well as the cluster type. As expected, the LC phase is stabilized by the addition of dendrons to the metallic cluster as already described for hexa-substituted fullerenes[6b] or polyhedral silsesquioxanes.[13g] Note that higher transition temperatures have been recorded for W_6 clusters when compared to Mo_6 clusters as a consequence of the presence of heavier and higher polarization of tungsten metal; a similar trend was reported for Mo and W liquid crystalline materials with no additional intermolecular interactions.[18] The POM observations (Figure 1) clearly indicate the formation of a layered SmA phase. Indeed, upon cooling the isotropic liquid, a clear fan-shape texture developed together with large homeotropic regions in the case of $\mathbf{MoL^2}$ and $\mathbf{WL^2}$, all indicative of a smectic A phase.

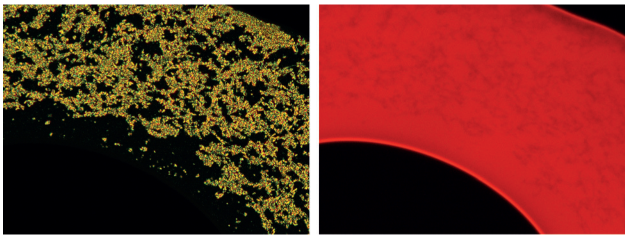


Figure 1. POM pictures of the SmA phase of $\mathbf{MoL^2}$ taken at 80 °C b) without and c) with irradiation in the 380–420 nm range.

Compounds $\mathbf{MoL^1}$ and $\mathbf{WL^1}$ show a rather sandy texture formed by shearing with high birefringent areas on cooling from the isotropic phase whereas compounds $\mathbf{MoL^3}$ and $\mathbf{WL^3}$ exhibit a fan-shape texture on heating near the decomposition temperature. These observations were confirmed by variable temperature 2D powder X-ray diffraction (Figures S34 and S35) recorded on cooling, with the exception of $\mathbf{MoL^3}$ and $\mathbf{WL^3}$, after a previous heating run above the clearing temperature. The XRD pattern of $\mathbf{MoL^3}$ and $\mathbf{WL^3}$ were recorded during the first heating run to prevent the decomposition above the clearing point. The temperature-dependent diffractograms show the same features for all compounds (Figures S28–S35). In the small-angle region, two or three sharp reflections in the 1:2:3 d-spacing ratio, were assigned to a long-range order of a layered phase. Additionally, the mesomorphic clusters $\mathbf{MoL^{1-3}}$ and $\mathbf{WL^{1-3}}$ exhibit one diffuse signal with the maxima located around 4.5 Å (h_{ch}) corresponding to the lateral short-range order of the molten alkyl chains. Another broad and intense reflection was found at the base of the sharp d_{002} reflection, around 20 Å ($h_{cluster1}$), for all six clusters that is associated with the average correlation distance between octahedral metallic cluster within the layers as already found in previously described LC Mo_6-based clusters or for LC SMM-based on dodecamanganese polyoxometalate.[8] The relative broadness of this reflection is indicative of a rather short-range order in intralayer corre-

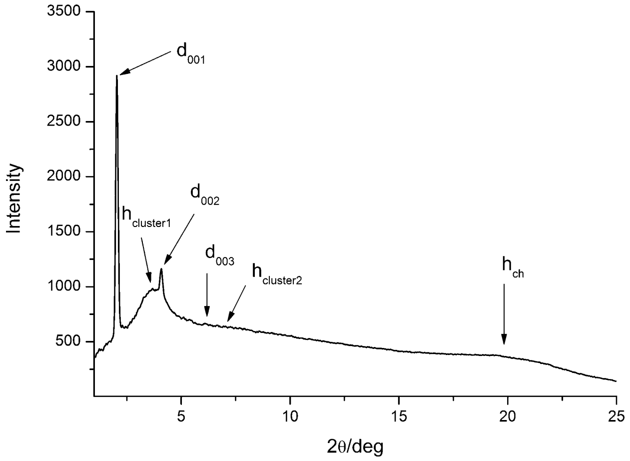


Figure 2. X-ray powder diffraction pattern for compound **WL^2** at 60 °C ($\lambda = 1.54$ Å).

lation between electron-rich cluster units. Interestingly, clustomesogens **MoL^2** and **WL^2** show another additional very broad reflection around 11–12 Å (h_{cluster2}) indicating some more local ordering within the clusters layer (Figure 2). However, again the absence of any other reflection and their broadness make any other assumption about intercluster organization difficult. The layer periodicity calculated for each compound at various temperatures is almost invariant suggesting that there is little influence of the temperature on the supramolecular packing within the mesophase. Several interesting correlations could be made for clusters **MoL^{2,3}** and **WL^{2,3}**. Thus, the layer periodicities of the metallic clusters do not differ too much from the one of phosphine oxide ligand itself, indicating a partially interdigitated packing within the mesophase and a minor contribution of the cluster units on the overall organization.

This point is also in good accordance with the assumption that ligand **L^2** and **L^3** self-arranges in a double-layer morphology. For instance, by molecular modeling of **L^2**, one arm of the star-shaped phosphine oxide ligand was found to measure in all-extended conformation around 37 Å whereas the rough diameter of the molecule stands for approximately 55 Å. Interestingly, the interlayer distances of metallic clusters **MoL^2** and **WL^2** (42.5–42.8 Å) are in fact slightly shorter than the one of corresponding ligand **L^2** (45.3 Å). Indeed, one can assume that now the cluster units are placed in the same sublayer with the triphenylphosphine oxide units. Such a packing could be interpreted as a double-layer morphology formed by cylindrical-shaped entities within the LC phase of metallic clusters. The cyanobiphenyl or cholesteryl mesogenic groups are placed on each side of the median plane determined by the metallic cluster units as we previously observed in our earliest clustomesogens and as it was found in structurally related nanohybrid materials of this type.[8,12c,19]

The Mo_6 and W_6 octahedral metallic cluster are well known for their broad emission in the near-infrared range (600–900 nm) upon UV-visible excitation, emission lifetimes in the microsecond range, and luminescence quantum yields higher than 60 %.[4,20] Generally, the photophysical properties of the clusters are dependent on both inner halide ligands X (X = Cl, Br, or I) in the cluster core and apical ligands. Thus, hexanuclear molybdenum and tungsten clusters with chlorine or bromide as inner ligands with various halides,[20] sulfonates,[21] carboxylates,[2a,3,4] or thiolates[22] in terminal positions were well studied for their red phosphorescence. On the other hand, to the best of our knowledge the emission properties of either Mo_6 or W_6 clusters with phosphine oxide as terminal ligands have never been reported although several such clusters have been prepared.[15,23] The emission properties were investigated in the liquid crystalline state with samples deposited on glass slides, heated to isotropic state and then cooled down slowly to room temperature by using a polarizing microscope equipped with a hotstage, an irradiation source (irradiation in the 380-420 nm range), and a CCD spectrophotometer. It was found that title clustomesogens, exhibit broad emission ranged from 550 up to 900 nm, with approx. 50 nm red-shifted maxima of emission for W_6-based clusters when compared to Mo_6-based clusters. The emission window is unaffected even in the isotropic phase at about the clearing point (Figure S53) whereas intensity slightly decreases upon heating. Moreover, the cluster compounds **MoL^4** and **WL^4** without mesogenic groups show the same characteristics of emission meaning that the introduction of mesogenic cyanobiphenyl or cholesteryl groups in the molecule does not affect the luminescence properties (Figure S54). Indeed, we demonstrated that utilizing various phosphine oxides as coordinating entities to the cluster core does not influence its emission properties. Furthermore, after functionalization with mesogenic groups these properties are preserved in the liquid-crystal state over the entire temperature range up to isotropic state.

In conclusion, we have demonstrated in this work that phosphine oxide cores functionalized with appropriate mesogenic groups can be successfully used as coordination entities to nanosized metallic clusters to generate LC properties, by varying both, their number density and position. The emissive properties of the cluster core are preserved in the LC state, even at higher temperatures and above the isotropization temperatures. Although we proved that phosphine oxide derivatives can be successfully coordinated to metallic clusters, we expect that, by careful design, they can be used in the preparation of various clustomesogens and more generally a wide variety of metallomesogens as such ligands are able to link to various metallic ions. This will open a new and exciting avenue for this class of compounds. Attempts are underway to utilize phosphine oxide modified with different mesogenic groups in order to finely tune the liquid-crystalline as well as emissive properties of these metal-based hybrid materials.

Keywords: cluster compounds · liquid crystals · molybdenum · phosphine oxide · tungsten

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