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Columnar Mesophases in Hybrid Organic−Inorganic Supramolecular Aggregates: Liquid Crystals of Fe, Cr, Mo, and W at Room Temperature, Built from Triazines and Metalloacid Complexes

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Hybrid organic−inorganic supramolecular aggregates displaying liquid crystal properties at room temperature have been synthesized by linking equimolar amounts of 2,4,6-triarylamino-1,3,5-triazine and metallo-acids [$Fe(CO)_4(CNC_6H_4CO_2H)$] and [$M(CO)_5(CNC_6H_4CO_2H)$] (M = Cr, Mo, W) through hydrogen bonding formation. The starting metalloacids and their triazine aggregates display photoluminescent properties in solution and in the condensed phase (crystalline or glassy) at low temperature, but not in the mesophase. The mesophase produced by the supramolecular hybrid aggregates is always columnar hexagonal (Col_h), corresponding to a columnar packing of 1:1 triazine-metalloacid supramolecules. The stability range of the columnar hexagonal mesophases is large, and the clearing temperatures decrease very regularly in the order Fe > Cr > Mo > W. All the supramolecular species show high thermal stability, even in the isotropic state.

Introduction

Intermolecular hydrogen bonding is a key attractive interaction stabilizing condensed phases and promoting molecular self-assembly. In the field of liquid crystals, it has been known since the early years of the 20th century that 4-alkoxybenzoic acids show liquid crystal behavior as a consequence of their self-assembling into dimers by hydrogen bonds.[1−3] There are many reports on the effects of intermolecular hydrogen bonding in the field of organic liquid crystals,[4] but only few cases in the field of metal-containing liquid crystals (metallomesogens),[5] namely, some hydrogen-bonded ferrocene complexes,[6−8] and a few phenanthroline copper derivatives.[9] Recently, we have reported some palladium, platinum, and gold isocyano complexes of 4-isocyanobenzoic acid. These complexes are metallo-acids and act as hydrogen donors to decyloxystilbazole through the carboxylic acid group, giving rise to supramolecular complexes that display liquid crystalline properties.[10,11] However, their thermal stability at the clearing temperatures is not high and the formation of some crystals is observed, revealing that the "clearing" transformation is not properly a phase transition without chemical change, but a collapse of the initial supramolecular structure, because of the thermal lability of the hydrogen bond.

Most mesogenic supramolecular structures reported show smectic mesophases, but there is a great interest in discotic liquid crystals due to the fact that columnar mesophases can display interesting electronic properties, for instance high charge carrier mobility along

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the columnar stacks.[12,13] A number of disk-like supramolecules formed through hydrogen bonding are known to display columnar mesophases. Among them, 2,4,6-triarylamino-1,3,5-triazines are useful bricks to form H-bonded aggregates with carboxylic acids that show columnar mesomorphism.[14−16]

Concerning metal containing liquid crystals (metallomesogens), many molecular systems displaying columnar mesophases have been described,[17] but to the best of our knowledge the above-mentioned phenanthroline copper derivatives[9] are the only report of columnar mesomorphism built through hydrogen bonding. On these grounds, it seemed that metal complexes containing as ligand the 4-isocyanobenzoic acid (metallo-acids) could be used to expand this type of columnar metallomesogens, by designing supramolecular structures with appropriate aspect, high thermal stability, and strong hydrogen bond interactions. The 2,4,6-triarylamino-1,3,5-triazines, which are known to give supramolecular liquid crystals by hydrogen bonding with carboxylic organic acids, and metalloacid complexes of the type $[M(CO)_n(CNC_6H_4CO_2H)]$ (Fe, Cr, Mo, W), were chosen as the building pieces that could provide thermally stable supramolecular aggregates. Moreover, the presence of carbonyl ligands on the metal could provide additional IR information on the aggregates as compared to the metal complexes.

Experimental Section

Experimental conditions for the analytical, spectroscopic, and diffraction studies were as reported elsewhere.[18] The IR spectra in the mesophase and in the isotropic liquid were recorded on neat compounds between polyethylene plates. Literature methods were used to prepare $[CNC_6H_4COOEt]$, $[C{\equiv}NC_6H_4COOH\text{-}p]$[10] and $[\{(C_{10}H_{21}O)_3C_6H_2NH\}_3C_3N_3]$.[15,19]

Preparation of $[Fe(CO)_4(CNC_6H_4COOH)]$ (1). To a solution of $[CNC_6H_4COOH]$ (0.3 g, 2.0 mmol) in tetrahydrofuran (30 mL) was added $[Fe(CO)_5]$ (0.45 mL, 4.0 mmol) under nitrogen. After refluxing for 45 min, the solvent was removed under vacuum. The resulting residue was chromatographed (silica gel, CH_2Cl_2 as eluent), and the solvent was evaporated to obtain the product as a orange solid (0.44 g, 70% yield). IR (KBr) $\nu(C{\equiv}N)$: 2162 s, $\nu(C{\equiv}O)$: 2061 s, 1951 (br, vs), $\nu(C{=}O)$: 1691 (m). ^1H NMR (THF-d_8): δ 7.47 (m, 2H, C_6H_4), 8.19 (m, 2H, C_6H_4). Anal. Calcd. for $C_{12}H_5FeNO_6$: C, 45.72; H, 1.60; N, 4.45. Found: C, 46.02; H, 1.78; N, 4.53.

Preparation of $[Cr(CO)_5(CNC_6H_4COOH)]$ (2). A solution of trimethylamine N-oxide (0.07 g, 1 mmol) in of MeCN (30 mL) was added to a suspension of $[Cr(CO)_6]$ (0.22 g, 1.0 mmol) in MeCN (30 mL) under nitrogen. The yellow solution formed was stirred for 3 h and the solvent was removed under vacuum. The residue was solved in tetrahydrofuran (20 mL) and a solution of $[CNC_6H_4COOH]$ (0.15 g, 1.0 mmol) in tetrahydrofuran (20 mL) was added dropwise. After stirring for 2 h the solvent was removed under vacuum to give the product as an orange solid (0.22 g, 66% yield). IR (KBr) $\nu(C{\equiv}N)$: 2139 (m), $\nu(C{\equiv}O)$: 2058 (s), 2000 (m), 1962 (sh), 1936 (vs), $\nu(C{=}O)$: 1696 (m). ^1H NMR (THF-d_8): δ 7.64 (m, 2H, C_6H_4), 8.12 (m, 2H, C_6H_4), 11.9 (s, broad, COOH). Anal. Calcd for $C_{13}H_5CrNO_7$: C, 46.04; H, 1.49; N, 4.13. Found: C, 45.86; H, 1.61; N, 4.38.

Preparation of $[M(CO)_5(CNC_6H_4COOH)]$ (M = Mo (3), W (4)). To a mixture of $[M(CO)_6]$ (M = Mo, W) (1.0 mmol) and $[CNC_6H_4COOH]$ (0.15 g, 1.0 mmol) in tetrahydrofuran (20 mL) was added dropwise a solution of trimethylamine N-oxide (0.078 g, 1,0 mmol) in 40 mL of dichloromethane under nitrogen. After stirring for 6 h, the solvent was removed under a vacuum. The resulting residue was extracted in diethyl ether (40 mL) and the solvent was evaporated to obtain the product as an orange solid. **M = Mo** (0.28 g, 72% yield): IR (KBr): $\nu(C{\equiv}N)$: 2132 (m), $\nu(C{\equiv}O)$: 2061 (s), 2007 (m), 1964 (sh), 1936 (vs), $\nu(C{=}O)$: 1699 (m). ^1H NMR (THF-d_8): δ 7.64 (m, 2H, C_6H_4), 8.12 (m, 2H, C_6H_4), 11.8 (s, broad, COOH). Anal. Calcd for $C_{13}H_5MoNO_7$: C, 40.76; H, 1.32; N, 3.66. Found: C, 41.03; H, 1.60; N, 3.59. **M = W** (0.39 g, 82% yield): IR (KBr): $\nu(C{\equiv}N)$: 2134 (m), $\nu(CO)$: 2061 (s), 2000 (m), 1952 (sh), 1926 (vs), $\nu(C{=}O)$: 1686 (m). ^1H NMR (THF-d_8): d 7.64 (m, 2H, C_6H_4), 8.12 (m, 2H, C_6H_4). Anal. Calcd for $C_{13}H_5WNO_7$: C, 33.15; H, 1.07; N, 2.97. Found: C, 33.42; H, 1.31; N, 3.13.

Preparation of $[W(CO)_5(CNC_6H_4COOEt)]$. To a mixture of $[W(CO)_6]$ (0.352 mg, 1.0 mmol) and $[CNC_6H_4COOEt]$ (0.018 g, 1.0 mmol) in tetrahydrofuran (20 mL) was added dropwise a solution of trimethylamine N-oxide (0.075 g, 1,0 mmol) in 40 mL of dichloromethane under nitrogen. After being stirred for 6 h, the solvent was pumped off in a vacuum. The resulting residue was extracted in diethyl ether (40 mL) and the solvent was evaporated affording the product as an orange solid. (0.31 g, 62% yield): IR (KBr): $\nu(C{\equiv}N)$: 2145 (m), $\nu(C{\equiv}O)$: 2061 (s), 1988 (m), 1952 (vs), 1923 (sh), $\nu(C{=}O)$: 1712 s. ^1H NMR (THF-d_8): δ 1.43 (t, 3H, $CH_2\mathit{CH_3}$), 4.43 (c, 2H, $\mathit{CH_2}CH_3$), 7.45 (m, 2H, C_6H_4), 8.13 (m, 2H, C_6H_4). Anal. Calcd for $C_{15}H_9WNO_7$: C, 36.10; H, 1.82; N, 2.81. Found: C, 36.46; H, 2.09; N, 3.02.

Preparation of Hydrogen-Bonded Triazine Complexes. The supramolecular complexes were all prepared from pure components. Exact stoichiometric molar amounts of the two compounds were dissolved in dry tetrahydrofuran at room temperature, and the solvent was pumped off in vacuum, affording the aggregates as orange viscous oils.

Results and Discussion

Synthesis and Characterization. The isocyanide-carbonyl compounds were prepared by selective substitution of one CO for CNC_6H_4COOH in the corresponding penta or hexacarbonyl complexes, as summarized in Scheme 1.

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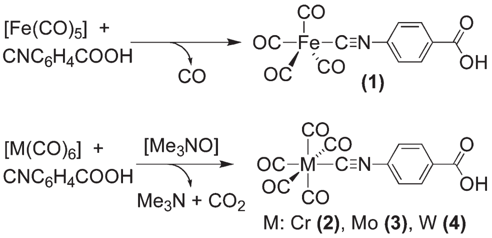
Scheme 1. Synthesis of Isocyanide Metal Complexes



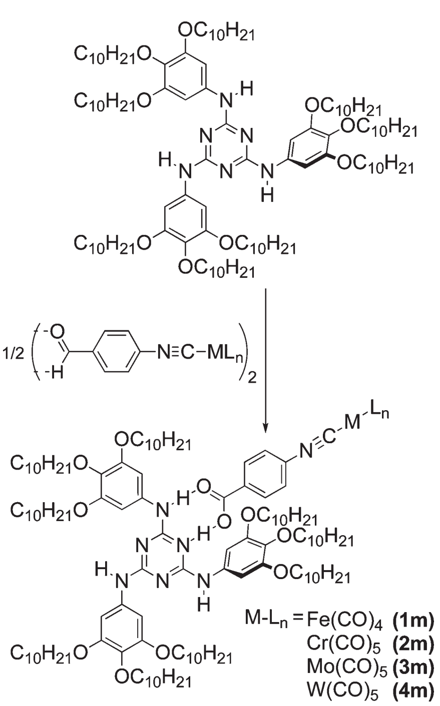
Complex $[Fe(CO)_4(CNC_6H_4COOH)]$ (**1**) was obtained directly by refluxing $[Fe(CO)_5]$ and $[CNC_6H_4COOH]$ in tetrahydrofuran, whereas $[M(CO)_5(CNC_6H_4COOH)]$ [M = Cr (**2**), Mo (**3**), W(**4**)] were prepared from $[M(CO)_6]$ and $[CNC_6H_4COOH]$ in the presence of trimethyl amine N-oxide, as reported for other similar systems.[20] All isocyanide metal complexes prepared are air stable orange solids.

C, H, N analyses for the complexes, yields, and relevant IR and NMR data are given in the experimental part. The IR spectra of $[Fe(CO)_4(CNC_6H_4COOH)]$ show one $\nu(C{\equiv}N)$ absorption for the isocyanide and three $\nu(C{\equiv}O)$ for the carbonyl groups, as expected for a trigonal bipyramidal structure with the isocyanide ligand coordinated in axial position (C_{3v} point-group symmetry).[21] The $\nu(C{\equiv}N)$ band appears at higher wavenumbers (ca. 35 cm^{-1}) than for the free isocyanide, as a consequence of coordination.[22] Similarly, the IR spectra of pentacarbonylisocyanide complexes $[M(CO)_5(CNC_6H_4COOH)]$ [M = Cr (**2**), Mo (**3**), W(**4**)] display one $\nu(C{\equiv}N)$ and three $\nu(C{\equiv}O)$ absorptions (A_1, B_1, E + A_1), as expected for their octahedral structure (C_{4v} point-group symmetry).[23] In addition, all the complexes display one $\nu(C{=}O)$ band from the carboxylic group at ca. 1695 cm^{-1}. This band is assigned to carbonyl-stretching vibration in the closed hydrogen-bonded dimeric form of the metalloacid, as reported for gold compounds with 4-isocyanobenzoic acid.[11] A broad $\nu(O{-}H)$ band at ca. 2980 cm^{-1} is also observed, as in the isocyanide ligand and their gold complexes.

The ^1H NMR spectra of all the complexes are similar and show, as expected, two resonances (AA′XX′ spin system) for the aryl protons of the isocyanide ligand. These signals are slightly shielded (0.04−0.11 ppm) from their position in the free isocyanide, except for $[Fe(CO)_4(CNC_6H_4COOH)]$ in which a slight shielding (0.07 ppm) is observed for the protons *ortho* to the isocyanide group. The acidic proton is observed at room temperature only for the Cr and Mo complexes, as a broad signal at 11.8 ppm. For the other complexes, the observation of the acidic H required cooling to 230 K.

Hydrogen-Bonded Triazine Complexes. The hydrogen-bonded triazine complexes were prepared by dissolving together equimolar proportions of the corresponding **1**−**4** compound and the triazine in THF at room temperature. Evaporation of the solvent in vacuum afforded **1m**−**4m** (Scheme 2) in quantitative yield, as orange waxy or oily materials. It is interesting to note, for later discussion, that the synthesis is antientropic (neglecting solvent interactions, 3 molecules react to produce 2 molecules), and hence it has to be enthalpy driven, meaning that the hydrogen bonds formed in the aggregate are stronger than the hydrogen bonds broken.

Scheme 2. Synthesis of the Supramolecular Triazine-Metalloacid Complexes



IR spectroscopy confirmed the quantitative formation of the supramolecular complexes **1m-4m** by the absence, in the isolated material, of some characteristic intense absorptions of the free components: the infrared spectra in the condensed[24] state do not show the $\nu(O{-}H)$ absorption of the precursors, and the $\nu(C{=}O)$and $\nu(C{\equiv}O)$ bands appear clearly shifted from their positions in the parent complexes. Changes in the region of $\nu(N{-}H)$ bands are also observed upon formation of the aggregate, as reported from triazine-organic acid aggregates.[15] Thus, the presence of unreacted materials can be safely excluded, even when the assignment of these $\nu(O{-}H)$, $\nu(N{-}H)$, and $\nu(C{=}O)$ bands in the triazine-matalloacid supramolecular complexes is not possible because of the low intensity and large width (for $\nu(O{-}H)$ and $\nu(N{-}H)$ absorptions), or to overlapping with the $\nu(C{=}N)$ triazine bands in the region 1660−1560 cm^{-1} with the $\nu(C{=}O)$ absorptions, which appear shifted at lower wavenumbers from their positions in the parent complexes.

The infrared $\nu(C{\equiv}O)$ bands associated to the metal carbonyl ligands also provide interesting information. Quantitative analysis of the intensity of the carbonyl

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(24) As the isolated materials are usually in LC state, we will use “condensed state” meaning the compound alone, usually LC state, and occasionally solid state, as different from the compound in solution.

Table 1. Selected Infrared Spectral Data in KBr Pellets (cm^{-1}) for the Metalloacids and Their Triazine Aggregates

	metalloacid			triazine aggregates[a]		
	$\nu(N\equiv C)$	$\nu(C\equiv O)$	$\nu(C=O)$	$\nu(N\equiv C)$	$\nu(C\equiv O)$	$\nu(C=O) + \nu(C=N)$
$[Fe(CO)_4(CNC_6H_4CO_2H)]$ (**1**)	2162 (m)	2061 (s) 1951 (vs)	1691 (m)	2158 (s)	2054 (s) 2000 (s) 1971 (vs)	1583 (s)
$[Cr(CO)_5(CNC_6H_4CO_2H)]$ (**2**)	2139 (m)	2058 (s) 2000 (m) 1962 (sh) 1936 (vs)	1696 (m)	2135 (m)	2052 (s) 2000 (m) 1962 (vs) 1936 (sh)	1596 (s)
$[Mo(CO)_5(CNC_6H_4CO_2H)]$ (**3**)	2132 (m)	2061 (s) 2007 (m) 1964 (sh) 1926 (vs)	1699 (m)	2135 (m)	2057 (s) 2002 (m) 1964 (vs) 1929 (sh)	1597 (s)
$[W(CO)_5(CNC_6H_4CO_2H)]$ (**4**)	2134 (m)	2059 (s) 2000 (m) 1952 (sh) 1926 (vs)	1686 (m)	2136 (m)	2052 (s) 1998 (m) 1957 (vs) 1927 (sh)	1596 (s)
$[W(CO)_5(CNC_6H_4CO_2Et)]$ (**5**)	2145 (m)	2061 (s) 1988 (m) 1952 (vs) 1923 (sh)	1712 (m)	2145 (m)	2061 (s) 1988 (m) 1960 (vs) 1924 (sh)	1718 (s) 1583 (s)

[a] Compound **5** does not form aggregates and the IR remains unchanged.

stretching vibrations is beyond the purpose of this analysis, but it is qualitatively known that π-bonding effects determine the infrared intensities of the CO modes in transition metal carbonyl compounds.[25−27] In $[M(CO)_5L]$ (M = Cr, Mo, W) and $[Fe(CO)_4L]$ species, the intensity of the A_1 mode (associated mainly to the CO trans to the L group) decreases for stronger π acid L groups that reduce the π-back-donation from the metal center to the carbonyl group.[28] In our compounds, this A_1 mode, associated with the stretching frequency of carbonyl group trans to the CNR ligand, corresponds to the lower wavenumber $\nu(C\equiv O)$ band in each complex;[29,30] it decreases significantly upon formation of the supramolecular aggregate (Table 1 and Figure 1), indicating that the isocyanide becomes stronger π acid upon implication of the carboxylic acid group in stronger hydrogen bonds.[31] Note that, as expected, when the complex has an ester group instead of a carboxylic acid (complex **5** in Table 1), aggregation does not occur, and the IR bands do not shift.

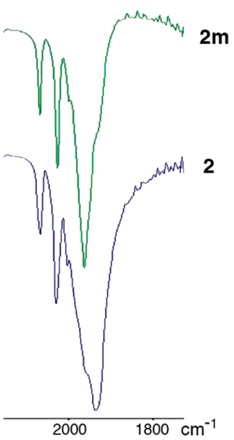

Figure 1. FTIR spectra in KBr pellets of $[Cr(CO)_5(CNC_6H_4CO_2H)]$ (**2**) and its triazine aggregate (**2m**).

The structure of the aggregates is clearly maintained in chloroform solution. Evidence from ^{1}HNMR spectra in $CDCl_3$ solution is, in this case, of little value, because the differences with the spectra of the two components are very small; for instance, the N−H proton appears as a singlet in the free triazine at 6.72 ppm, which is broadened and slightly shifted to lower field upon H-bonding complexation (6.75 for **4m**). However, the IR evidence is compulsive: the pattern and the position of the $\nu(C\equiv O)$ bands is almost identical to the IR spectrum of the material in the condensed phase (mesophase), both in CH_2Cl_2 solution and in the isotropic phase obtained from the mesophase upon heating; this supports that the supramolecular aggregate persists in all these conditions (Table 2).[32]

Mesogenic Behavior. The triazine used in this work $[\{(C_{10}H_{21}O)_3C_6H_2NH\}_3C_3N_3]$ displays a columnar hexagonal mesophase at room temperature, with a clearing transition to isotropic at 57 °C.[33] The metalloacids **1−4** have a reasonable thermal stability, but are not mesomorphic. They decompose progressively, without melting, above 180 °C. All the supramolecular triazine-metalloacid aggregates **1m−4m** display enantiotropic

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(30) Although B_1 is not IR active, it is often observed in this type of complexes. See: Reckziegel, A.; Bigorgne, M. *J. Organomet. Chem.* **1965**, *3*, 341–354.
(31) Remember that, as discussed above, the hydrogen bonds formed in the melamine aggregate are stronger than the hydrogen bonds in the dimeric metalloacid.
(32) In solution, small variations in the intensity of the different bands produce small changes in the aspect of the spectrum, but in no case bands associated to the individual molecules composing the supramolecules are observed.
(33) This triazine has been described in ref 15. However, there is a significant discrepancy between the reported clearing temperature and that measured in this work.

Table 2. Selected Infrared Spectral Data for Triazine Aggregates 1m−4m

triazine aggregates	IR (cm^{-1})					
	CH$_2$Cl$_2$		mesophase (50 °C)		isotropic liquid (95 °C)	
	ν(N≡C)	ν(C≡O)	ν(N≡C)	ν(C≡O)	ν(N≡C)	ν(C≡O)
1m	2162 (m)	2055 (s)	2157 (m)	2054 (s)	2153 (m)	2053 (s)
		1998 (m)		2000 (m)		1999 (m)
		1967 (vs)		1972 (vs)		1973 (vs)
2m	2138 (m)	2055 (s)	2134 (m)	2054 (s)	2132 (m)	2051 (s)
		2000 (m)		2000 (m)		2000 (m)
		1959 (vs)		1964 (vs)		1965 (vs)
				1929 (sh)		1932 (sh)
3m	2138 (m)	2059 (s)	2133 (m)	2056 (s)	2130 (m)	2055 (s)
		2000 (m)		2004 (m)		2007 (m)
		1959 (vs)		1966 (vs)		1964 (vs)
				1926 (sh)		1926 (sh)
4m	2139 (m)	2055 (s)	2133 (m)	2051 (s)	2131 (m)	2050 (s)
		2000 (m)		1994 (m)		1996 (m)
		1953 (vs)		1960 (vs)		1960 (vs)
				1928 (sh)		1928(sh)

Table 3. Optical, Thermal, and Thermodynamic Data of 1m−4m

compd	transition[a]	temperature[b] (°C)	ΔH[b] (kJ/mol)
melamine	Col$_h$ → I	57	2.0
1m (Fe)	Cr → Col$_h$	8	3.6
	Col$_h$ → I	86	14.3
2m (Cr)	Col$_h$ → I	84	37.1
3m (Mo)	Col$_h$ → I	80	20.9
4m (W)	Col$_h$ → I	77	15.5

[a] Cr, crystal; Col$_h$, columnar hexagonal; I, isotropic liquid. [b] Data collected from the second heating DSC cycle. The transition temperatures are given as peak onsets.

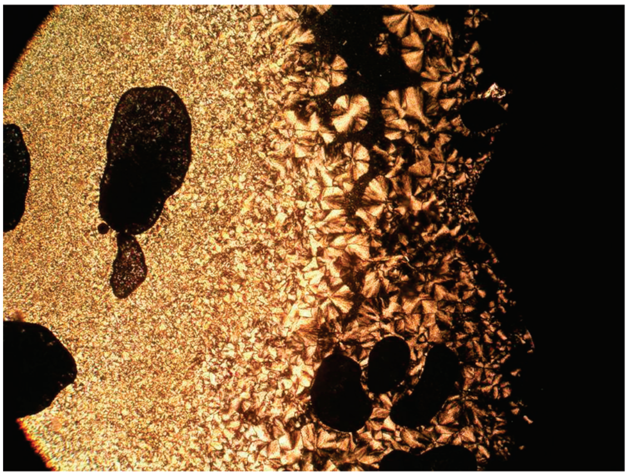

Figure 2. Polarized optical microscopic texture (× 100) observed for **2m** on cooling from the isotropic liquid at 75 °C.

liquid crystal behavior at room temperature up to ca. 80 °C; therefore, a substantial stabilization of the mesophases was achieved upon the association of the metalloacids to the melamine derivative. The mesophases were studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS). The optical, thermal, and thermodynamic data are collected in Table 3.

The compounds **1m−4m** have a fairly large mesophase temperature domain from about 80 °C down to below room temperature. The fluid and homogeneous optical textures, when viewed with a polarizing microscope on cooling from the isotropic melt, are characteristic of a columnar organization: pseudo focal conic fanlike optical defect along large homeotropic regions are displayed and it is possible to shear the sample easily by mechanical stress, suggesting strongly a columnar phase with hexagonal symmetry as the precursor triazine (Figure 2).[34] In general the mesophases freeze at low temperatures, and the transition fluid-to-solid is difficult to determine (peak is not detected by DSC either), suggesting the transformation into the glass state. Crystallization is observed for the Fe compound **1m** only and detected in the DSC by a sharp endothermic peak.

The supramolecular aggregation of triazine with metalloacids to give the supramolecular complexes **1m−4m** produces an increase in the mesophase range and stability compared to that of the free triazine. The stability of the columnar hexagonal mesophase formed is high, as reflected by the high enthalpy values measured for the Col$_h$−I transition (Table 3). Similar high energy values have been reported for analogous triazine aggregates with organic acids.[15,16]

The triazine-metalloacid supramolecular complexes have remarkable thermal stabillity and no apparent decomposition is observed, even in the isotropic state. This is in contrast to hydrogen-bonded supramolecular liquid crystals based on 4-isocyanobenzoic acid derivatives of gold, palladium, and platinum with decylstilbazole, which decompose at the clearing temperatures.[10,11] This different thermal behavior is due to the metal complex component of the supramolecule, which is thermally labile for the Au complex, but very stable for **1−4**. However, the question remains whether the supramolecules persist in the isotropic liquid or are split into their individual components. Interestingly, the clearing points decrease very regularly in the order Fe > Cr > Mo > W, in coincidence with the increase of the radius of the metallic atom in the order Fe < Cr < Mo < W.[35] This

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Table 4. Structural Data from X-ray Diffraction Experiments

		indexation			
compound, T (°C)	d_{meas} (Å)[a]	hk[b]	I[c]	d_{calcd} (Å)[a]	params[d]
m, 30	25.83	10	VS (sh)	25.83	$a = 29.85$ Å
	4.4	h_{ch}	VS (br)		$S = 770$ Å^2
					$V_{\text{mol}} = 2925$ Å^3
					$N = 1$ for $h = 3.8$ Å
1m, 50	27.05	10	VS (sh)	26.96	$a = 31.13$ Å
	15.66	11	M (sh)	15.56	$S = 840$ Å^2
	13.36	20	M (sh)	13.48	$V_{\text{mol}} = 3450$ Å^3
	4.5	h_{ch}	VS (br)		$N = 1$ for $h = 4.1$ Å
2m, 30	27.23	10	VS (sh)	27.17	$a = 31.37$ Å
	15.84	11	M (sh)	15.69	$S = 852$ Å^2
	13.43	20	M (sh)	13.59	$V_{\text{mol}} = 3490$ Å^3
	4.5	h_{ch}	VS (br)		$N = 1$ for $h = 4.1$ Å
3m, 30	27.45	10	VS (sh)	27.45	$a = 31.70$ Å
	4.5	h_{ch}	VS (br)		$S = 870$ Å^2
					$V_{\text{mol}} = 3560$ Å^3
					$N = 1$ for $h = 4.1$ Å
4m, 30	27.42	10	VS (sh)	27.42	$a = 31.66$ Å
	4.5	h_{ch}	VS (br)		$S = 868$ Å^2
					$V_{\text{mol}} = 3705.1$ Å^3
					$N = 1$ for $h = 4.3$ Å

[a] d_{meas} and d_{calc} are measured and calculated periodicities. [b] Miller indices, hk; I corresponds to the intensity of the reflections (VS: very strong, M: medium; br and sh: broad and sharp); h_{ch} represents the molten chain short-range distance. [d] Phase parameters: intercolumnar distance, $a = 2 \times [\Sigma d_{hk}\sqrt{(h^2 + k^2 + hk)}]/\ N_{hk}\sqrt{3}$; number of reflections, N_{hk}; columnar cross-section of the hexagonal cell, $S = 1/2a^2\sqrt{3}$; V_{mol}, molecular volume, is determined considering a density of 1 according to $\text{MW}/(6.022 \times 10^{23})(1 \times 10^{-24})$, where MW is the molecular weight. The repeating columnar unit h is defined as NV_{mol}/S, where N is set equal to 1 (one molecular equivalent per repeat unit).

suggests that, most likely, the collapse of the columnar order to an isotopic liquid is not produced by a splitting of the hydrogen bonds in the supramolecule, and the clearing points are related to some steric effect. The stability of the supramolecular aggregate upon clearing is supported by the fact that no significant changes are observed in the IR spectra of the materials in KBr pellets at room temperature, in the mesophase at 50 °C and in the isotropic liquid state at 95 °C. The survival of the supramolecular structure in all te phases is, then, the most likely proposal. Moreover, in case splitting of the hydrogen bonds in the supramolecule would be happening one might expect the formation of solid **1**−**4**, which is not observed.

X-ray Diffraction Experiments. Temperature-dependent X-ray diffraction experiments were systematically carried out in order to unequivocally identify the nature of the mesophase. The X-ray patterns of the supramolecular aggregates of Fe and Cr recorded between room temperature and ca. 80 °C exhibited three sharp and intense small angle diffraction peaks with a reciprocal d spacing in the ratio $1{:}\sqrt{3}{:}\sqrt{4}$. These features are most readily assigned to the (10), (11) and (20) reflections of a columnar phase with hexagonal lattice, in agreement with POM observations. In addition, a strong and diffuse halo at 4.5 Å was observed and assigned to the liquidlike order of the molten alkoxy chains. The supramolecular aggregates of Mo and W appeared less stable and were found to decompose/dissociate quicker than the Cr homologue upon X-ray beam exposition (this decomposition was not observed under POM or DSC conditions). As a consequence of this partial decomposition under X-ray observation, the X-ray patterns presented two sets of peaks, indicative of the coexistence of phases: peaks corresponding to the minor crystalline phase (crystallization of the dissociated organometallic fragment) arising from dissociation, and major peaks associated with the liquid crystalline hexagonal lattice of the adducts. As they were observed in **1m** and **2m**, it was possible to tentatively assign the diffraction peaks (10), (11), and (20). In the latter cases the nature of the mesophase was determined based on the analogies in the textures observed by POM and in the diffraction patterns. Thus, the insertion of the metalloacid fragment within the core of the triazine is not detrimental to mesomorphism, as the phase nature is kept unchanged, because a Col_h phase is observed in both cases. Moreover, the stability of the mesophases is substantially enhanced by the increase of the isotropization temperature by nearly 50 °C. The observation of higher-order reflections in the diffraction patterns of the complexes when compared to that of the ligand suggest a higher degree of supramolecular organization in the former, likely due to an enhanced rigidity of the supramolecular ensemble and electronic density, resulting in more efficient intermolecular interactions and packing; this result is also consistent with the values of the transition enthalpies found for the complexes. Structural data from X-ray diffraction experiments are collected in Table 4.

As can be seen from these data, when comparing **m** and **_i_m** compounds, the later show a perturbed dislike aspect (Figure 3, left) The bulkiness of the metallic fragment within the ensemble affects, although not greatly, the dimensions of the columnar repeat unit: the thickness of the column (h) increases only from 3.8 to 4.1−4.2 Å from the free base to the metallo adducts; the columnar cross-section, S, expands as well, from 770 to 840−870 Å^2. This supports that the regular decrease of the clearing points observed in the order Fe > Cr > Mo > W is, as suggested before, a consequence of a steric effect. A slight expansion of the

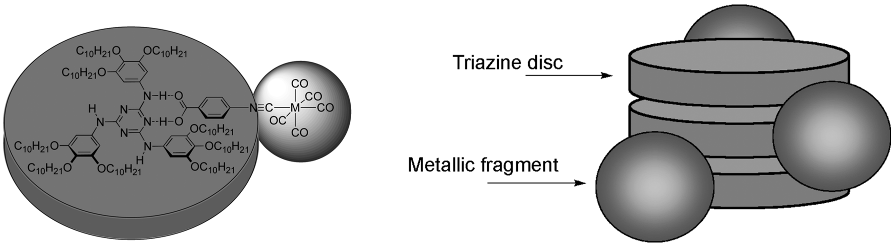

Figure 3. Perturbed disklike aspect of the triazine-metalloacid aggregate (left), and columnar structure of the mesophase (right). Depicted for M = Cr, Mo, W.

Table 5. UV-Visible Data of Metal Carbonyl Isocyanide Complexes

compound	λ (nm) (ε (dm^{3}mol^{-1}cm^{-1}))		
m[a]		283 (53000)	
1	276 (14400)		
2	240 (36300)		362 (8100)
3	241 (53500)		365 (9400)
4	240 (53300)		362 (7400)
1m		282 (65500)	
2m		280 (68800)	365 (16300)
3m	242 (115257)	280 (129200)	362 (10600)
4m	241 (118667)	278 (149200)	363 (10800)

[a] Free triazine.

Table 6. Emission and Excitation Maxima (nm) of the Metal Complexes

	$CHCl_3$ (298 k)		KBr (77.3 k)	
compd	λ_{ex}	λ_{em}	λ_{ex}	λ_{em}
m*	259	375	334	425
1	264	375		
2	266	376		
3	266	374	411	532
4	265	375	416	535
1m	257	372		
2m	266	380		
3m	267	376	397	531
4m	258	394	411	531

elementary repeat unit is also noticeable as a function of the metal complex size. Therefore, a plausible model is to consider that one supramolecular equivalent fills the elementary disk, and that the pending metallic fragment is randomly connected to the central core (three equivalent positions). The triazine parts are likely stacked on top of each other in a staggered manner (i.e., a mean rotation of the molecular plane by ca. 60°) in order to reduce the steric constraints, to neutralize the lateral dipoles, and to fill the space available between the branches by the neighbored trialkoxyphenyl moieties (Figure 3, right).

Photophysical Studies. The electronic spectra of metal complexes and the aggregates are collected in Table 5. They are all very similar, displaying two intense absorption bands at ca. 240 and 365 nm in $CHCl_3$ solution. According to the wavelengths and extinction coefficients, the band at 240 nm is typical of a ligand-centered $\pi-\pi^*$ transition associated to the aromatic groups, as reported for gold complexes of 4-isocyanobenzoic acid.[11] The band at 365 nm is assigned to a metal-to-ligand charge transfer transition (MLCT), as reported for related phenyl isocyanide Cr, Mo and W complexes.[36] Moreover, in the supramolecular triazine-metal complexes, an intense absorption band at ca. 280 nm corresponds to the triazine fragment and shows larger extinction coefficients than for the free triazine.

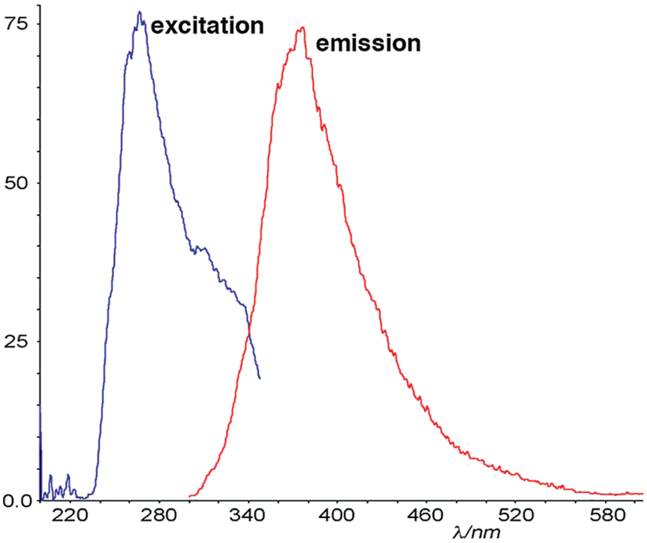

Figure 4. Luminescence excitation and emission spectra of **3** in $CHCl_3$ solution at room temperature. Emission intensity in arbitrary units.

The luminescence data of metal complexes are given in Table 6. In solution at room temperature, all the metal complexes (whether molecular or supramolecular) are luminescent and display a broad emission band at ca. 375 nm (Figure 4), but not in their condensed phases (crystal or mesophase). This is a very common phenomenon, which was also observed for the free isocyanide.[11]

At low temperature in the condensed state (crystal for **1**−**4** and **1m**, probably frozen glass for the rest), the complexes for the two first row transition metals (Fe and Cr) are not luminescent. In contrast, the Mo and W complexes show intense yellow-green luminescence (Table 4), which is visually observed under UV irradiation at 365 nm. The emission spectra consist of one strong not structured emission band with the maximum in the range 532−535 nm, assigned to a metal-to-ligand charge-transfer (MLCT), as reported for analogous isonitrile complexes.[37,38] The lifetime measured for [$W(CO)_5(CNC_6H_4COOH)$] in the solid state (53.9 μs) supports a phosphorescent nature for the emission. The nonemissive behavior of the Fe and Cr

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complexes compared to that of Mo and W might be associated with low spin−orbit coupling. In general, spin−orbit coupling facilitates, in metal complexes of second and third transition series, the observation of the spin-forbidden transitions that are not observed in similar metal complexes of first transition series. Similar results have been reported for Cr(0), Mo(0) and W(0) isocyanide octahedral complexes.[36]

In summary, we have prepared uncommon luminescent metalla-acids based on carbonyl iron, chromium, molybdenum, and tungsten complexes with 4-isocyanobenzoic acid and their hydrogen-bonded, supramolecular triazine-metalloacid complexes. All supramolecular hybrid aggregates obtained display interesting columnar mesophases with pending metallic fragments at room temperature. The stability range of the columnar hexagonal mesophases is larger in the aggregates than in the free triazine, and the clearing temperatures decrease very regularly in the order Fe > Cr > Mo > W. The supramolecular species show high thermal stability, even in the isotropic state.

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