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# From tectons to luminescent supramolecular ionic liquid crystals

Pierre Dechambenoit<sup>a,c</sup>, Sylvie Ferlay<sup>a\*</sup>, Bertrand Donnio<sup>b</sup>, Daniel Guillon<sup>b</sup> and Mir Wais Hosseini<sup>a\*</sup>

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**New phosphorescent and room-temperature liquid-crystalline materials were obtained by combining dicyanometallate anions with dicationic bisamidinium based tectons bearing four peripheral lipophilic pyrogallate moieties.**

Liquid crystals (LCs) constitute a class of soft materials, combining order with fluidity within various types of mobile and low-dimensional periodic structures.<sup>1</sup> Their dynamic nature, function-integration and stimuli-responsiveness abilities render them interesting for technological applications.<sup>2</sup> However, the control of self-assembling and self-organizing processes from functional nano-segregated structures to micrometric scale by molecular engineering still remains a challenge. Over the last two decades, the supramolecular approach, based on molecular recognition events,<sup>3</sup> has been considered<sup>4</sup> for generating novel LC assemblies integrating new functions. The majority of reported supramolecular LCs is mainly based on the use of non-ionic<sup>5</sup> or ionic<sup>6</sup> H-bonding.

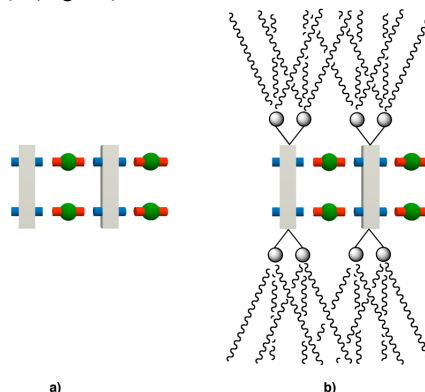
Functional mesophases displaying emissive properties are mostly achieved using either purely organic luminophores<sup>7</sup> or transition metal<sup>8</sup> and lanthanide<sup>9</sup> complexes. Hereafter, we report on new phosphorescent LC materials elaborated by molecular tectonic, an approach until now sparingly used in this area.



**Scheme 1**

Molecular tectonics,<sup>10</sup> a strategy allowing the assembly of molecular building blocks (tectons) into pre-designed 1-3D periodic architectures in crystalline phases or on surfaces,<sup>11</sup> seems particularly well-suited for the generation of LCs based on the formation of molecular networks composed of at least one mesogenic tecton. Indeed, using charge-assisted H-bonding,<sup>12</sup> it was shown that dicationic bisamidinium-based tectons combined with alkoxybenzoates lead to the formation of LC mesophases.<sup>6c</sup> Moreover, association of such dicationic tectons with cyanometallate anions induces the formation of porous networks in the crystalline phase.<sup>13</sup> In particular, the combination of compound **1**<sup>2+14</sup> (Scheme 1) with  $M(CN)_2^-$  ( $M = Ag$  or  $Au$ ) leads to the formation of neutral 1D H-bonded

networks (Fig. 1a).<sup>15</sup> The formation of the latter results from both electrostatic charge-charge interactions and directional H bonds between the acidic H atoms of **1**<sup>2+</sup> and N atoms of  $CN$  ligands of  $M(CN)_2^-$ . Furthermore, analogues of **1**<sup>2+</sup> bearing alkyl chains **2**<sup>2+</sup> (propyl<sup>16</sup>, hexyl or dodecyl groups) were found to behave in a similar fashion, demonstrating that the presence of alkyl substituents at these two positions do not alter the recognition pattern observed between the dication and  $M(CN)_2^-$  (Fig. 1a).<sup>17</sup>



**Figure 1:** Schematic representation of 1D H-bonded networks (ladder-like type) formed upon combination of the dicationic organic tecton **1**<sup>2+</sup> (a) or lipophilic **3**<sup>2+</sup> (b) with dicyanometallates.

In order to avoid crystallization and to induce the formation of mesophases, while maintaining the formation of 1D networks (Fig. 1b), the dicationic tecton **3**<sup>2+</sup> bearing four peripheral lipophilic pyrogallate units (Scheme 1) was considered as an appropriate unit to be combined with  $M(CN)_2^-$ .

As stated above, the design of **3**<sup>2+</sup> is based on the tetra H-bond-donor-unit bisamidinium central core bearing four mesogenic 3,4,5-trisalkoxybenzyl groups offering 12 flexible chains disposed in a symmetrical fashion. The phenyl spacer connecting the two cyclic amidinium moieties was chosen because not only it increases considerably the stability of the tecton towards hydrolysis but in addition it imposes the required distances between the two acidic H atoms on each face of the tecton and thus a distance of *ca* 4.0-4.2 Å between the two metal centers ( $Ag$  or  $Au$ ) and furthermore enhances that axial anisotropy of the system. This rather short M-M distance of *ca* 4.0-4.2 Å leads to metallophilic interactions<sup>18</sup> between adjacent metallic centers ( $Ag$  or  $Au$ ).

The interconnection of the mesogenic unit to the cyclic amidinium moieties was achieved using positions 1 and 4 of the phenyl group and the position 3 on the cyclic amidinium moiety. The junction between the rigid and flexible units was

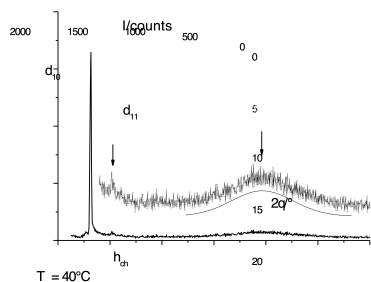
an ether group. As for the length of the alkyl chain, the dodecyl fragment was chosen.

The detailed synthetic strategy as well as preparative procedures for  $[3^{2+}][Cl^-]_2$  and  $[3^{2+}][Ag(CN)_2^-]_2$  are given in ESI.

The mesomorphic behaviour of  $[3^{2+}][X^-]_2$  ( $X = Cl$  or  $Ag(CN)_2$ ) was analyzed by polarized optical microscopy (POM), differential scanning calorimetry (DSC, figure S1 for  $[3^{2+}][Cl^-]_2$  and S2 for  $[3^{2+}][Ag(CN)_2^-]_2$  in ESI) and small-angle X-ray scattering (SAXS). As deduced by POM and DSC,  $[3^{2+}][Cl^-]_2$  and  $[3^{2+}][Ag(CN)_2^-]_2$  self-organize into fluid liquid crystalline mesophases from RT to 80 °C and 110 °C, respectively (for the latter compound, the glass transition temperature ( $T_g$ ) was detected during the first heating at 64 °C, but not on subsequent cycles). As expected, the large number of divergent chains on the cations are responsible for the low melting-temperature behaviour.<sup>19</sup> In both cases, the mesophases optical textures were birefringent and homogeneous but not sufficiently characteristic, prohibiting definitive mesophase assignments.

Temperature-dependent SAXS experiments confirmed and allowed LC phases' symmetry identification (Table 1). Both appeared as disordered mesophases as shown by the rather strong and diffuse signal in the wide-angle region (at around 4.5–4.6 Å) reflecting the liquid-like state of the molten alkyl chains. For  $[3^{2+}][Cl^-]_2$ , in the low angle region, several sharp and intense reflections are observed indicating the presence of 2D columnar arrangements, as shown in figure S3 (see ESI). At 40 °C, up to 8 sharp reflections were observed. Their indexation satisfied the conditions for the non-centered rectangular  $p2gg$  planar group ( $Col_r$ ) (figure S3, ESI).

For  $[3^{2+}][Ag(CN)_2^-]_2$ , at 40 °C, the X-ray pattern was composed of two sharp signals, shown in figure 2, with reciprocal d-spacing in the ratio 1:√3. This is compatible with the assignment of the two peaks as (10) and (11) reflections of the 2D hexagonal lattice with  $p6mm$  planar group ( $Col_h$  phase). (figure 2)



**Figure 2:** Small-angle XRD diffraction pattern and peaks indexation for  $[3^{2+}][Ag(CN)_2^-]_2$ , recorded at 313 K, second heating (Gaussian fit of the diffuse scattering halo). Considering a mean density of  $ca\ 1\ g\ cm^{-3}$  for both salts in their respective phase, about one molecular equivalent ( $[3^{2+}][Cl^-]_2$ ) or one elementary repeat unit ( $[3^{2+}][Ag(CN)_2^-]_2$ ) occupies the elementary columnar slice 4.5–4.6 Å-thick (Table 1). The specific Ag-Ag distances (in the  $20^\circ < 2\theta < 25^\circ$  range) cannot be detected by X-Ray diffraction, due to the presence of the diffuse and intense signal corresponding to the molten chains.

**Table 1:** Mesomorphic behaviour and mesophase structural data for  $[3^{2+}][X^-]_2$ . Temperatures in °C,  $\square H$  in  $kJ\ mol^{-1}$ , and  $\square Cp$  in  $J\ mol^{-1}\ K^{-1}$  (glass transition).

| Mesomorphic behaviour <sup>[a]</sup> | $d_{exp}/\text{\AA}$ <sup>[b]</sup> | $I^{[c]}$ | $hk$ <sup>[d]</sup> | $d_{theo}/\text{\AA}$ <sup>[b]</sup> | Parameters <sup>[e]</sup> | $h/\text{\AA}^{[e]}$ , $N$ |
|--------------------------------------|-------------------------------------|-----------|---------------------|--------------------------------------|---------------------------|----------------------------|
| $[3^{2+}][Cl^-]_2$                   | 34.1                                | VS (sh)   | 11                  | 34.1                                 | $T = 40^\circ\text{C}$    | $V_{mol} =$                |
|                                      | 30.45                               | M (sh)    | 20                  | 30.45                                | $Col_r-p2gg$              | 4800                       |
| Cr -12 (42.5)                        | 19.75                               | M (sh)    | 12                  | 19.5                                 | $a = 60.9\ \text{\AA}$    | $\text{\AA}^3$             |
| $Col_r-p2gg$ 80                      | 17.05                               | M (sh)    | 22                  | 17.05                                | $b = 41.15\ \text{\AA}$   | $N \sim 1$                 |
| (3.3) I                              | 15.6                                | W (sh)    | 40                  | 15.22                                | $S = 2506\ \text{\AA}^2$  |                            |
|                                      | 11.26                               | W (sh)    | 33                  | 11.37                                |                           |                            |
|                                      | 9.5                                 | M (sh)    | 24                  | 9.75                                 |                           |                            |
|                                      | 8.55                                | M (sh)    | 44                  | 8.52                                 |                           |                            |
|                                      | 4.5                                 | VS (br)   |                     | $h_{ch}$                             |                           |                            |
| $[3^{2+}][Ag(CN)_2^-]_2$             | 29.87                               | VS (sh)   | 10                  | 29.85                                | $T = 40^\circ\text{C}$    | $V_{mol} =$                |
|                                      | 17.22                               | W (sh)    | 11                  | 17.23                                | $Col_h-p6mm$              | 4950                       |
| g (2.7) 64 $Col_h$                   | 4.6                                 | VS (br)   |                     | $h_{ch}$                             | $a = 34.46\ \text{\AA}$   | $\text{\AA}^3$             |
| 110 (-) <sup>[f]</sup> I             |                                     |           |                     |                                      | $S = 1029\ \text{\AA}^2$  | $N \sim 1$                 |

Abbreviations: <sup>[a]</sup> $Col_h$  = hexagonal columnar phase;  $Col_r$  = rectangular columnar phase; Cr = crystalline phase; g = glass; I = isotropic liquid.

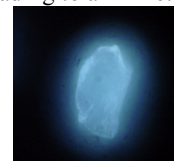
<sup>[b]</sup> $d_{exp}$  and  $d_{theo}$  are the experimentally measured and theoretical diffraction spacings. The distances are given in Å. <sup>[c]</sup>Intensity of the reflections: VS: very strong, M: medium, W: weak; br and sh stand for broad and sharp reflections, respectively. <sup>[d]</sup> $hk$  are the Miller indices of the reflections<sup>20</sup>.

<sup>[e]</sup>Mesophases parameters  $a$ ,  $b$ ,  $S$ , are deduced from the following mathematical expressions. For  $Col_h$ , the lattice parameter  $a = 2[\square_{hk}d_{hk} \cdot (h^2 + k^2 + hk)^{1/2}] / \sqrt{3N_{hk}}$  where  $N_{hk}$  is the number of  $hk$  reflections, and the lattice area (*i.e.* columnar cross-section)  $S = a^2\sqrt{3}/2$ . For  $Col_r$ ,  $\langle d_{hk} \rangle = 1/[(h^2 + a^2/k^2 + b^2)^{1/2}]$ , the lattice area  $S = a \times b$  (columnar cross-sections =  $S/2$ ).  $N$  is the number of molecules (or molecular equivalents):

$N = h_{ch} \cdot S / V_{mol}^{21}$  where  $S$  is the columnar cross-section,  $V_{mol}$  is the molecular volume (estimated with a density close to 1) and  $h_{ch}$  the average thickness of the molecule for repeating stacking distance along the column (*i.e.* the diffuse scattering corresponding to the molten aliphatic chains). <sup>[f]</sup>Transition not detected by DSC, but by POM and

XRD.

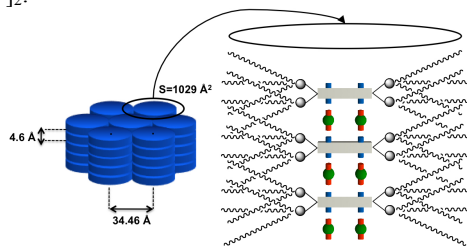
As previously observed for  $[1^{2+}][Ag(CN)_2^-]_2$  in the crystalline phase,<sup>15</sup> the mesophase generated by  $[3^{2+}][Ag(CN)_2^-]_2$  also displays luminescence (Fig. 3). Indeed, excitation of  $[3^{2+}][Ag(CN)_2^-]_2$  at 380 nm leads to blue luminescence at 430 nm. In contrast, no emission is observed for  $[3^{2+}][Cl^-]_2$  implying probably that the luminescence is related to Ag-Ag interactions.<sup>22</sup> Moreover, the mesogenic structural changes between  $[3^{2+}][Cl^-]_2$  and  $[3^{2+}][Ag(CN)_2^-]_2$  clearly indicates a different packing for the latter, involving H bonds and formation of the already observed recognition mode between cations and anions, leading to a 1D network.<sup>15</sup>



**Figure 3:** Photomicrograph showing the blue luminescence of the  $[3^{2+}][Ag(CN)_2^-]_2$  mesophase.

For  $[3^{2+}][Ag(CN)_2^-]_2$ , based on X-ray and luminescence data, the following model for the  $Col_h$  phase may be proposed: disks made of a single organic mesogenic tecton  $3^{2+}$  are interconnected by  $Ag(CN)_2^-$  through both H-bonds between acidic H atoms of  $3^{2+}$  and CN groups of the cyanometallate and electrostatic interactions forming thus neutral 1D ladder-type networks (Fig. 1b). The latter, surrounded by flexible alkyl chains (Fig. 4), pack into a 2D hexagonal lattice where the relative orientations (*ie* defined by the normal axis of the

1-D network) of the molecular ladders are not necessarily correlated with neighbouring columns of the hexagonal network. This model also agrees with the enhanced thermal stability observed for  $[3^{2+}][Ag(CN)_2^-]_2$  with respect to  $[3^{2+}][Cl^-]_2$ .



**Figure 4:** Proposed columnar model based on the interconnection of disks composed of  $3^{2+}$  by  $Ag(CN)_2^-$ .

## Conclusions

The combination of the mesogenic dicationic tecton  $3^{2+}$ , bearing 12 divergently oriented C12 aliphatic chains, with  $Ag(CN)_2^-$  leads to the formation of a supramolecular 1D charge-assisted H-bonded network displaying columnar mesophase properties in a wide temperature range. The columnar mesophase might result from interconnections of disks composed of  $3^{2+}$  by  $Ag(CN)_2^-$  through both H-bonds and electrostatic interactions. The imposed rather short Ag-Ag distance through the design of the organic tecton  $3^{2+}$  is probably responsible for the observed blue luminescence of the mesophase. The extension of this approach to other organic mesogens and metal complexes is currently under investigation.

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## Notes and references

<sup>a</sup> Laboratoire de Chimie de Coordination Organique, UMR CNRS 7140, Université de Strasbourg, Institut Le Bel, 4, rue Blaise Pascal, CS 90032 67081 STRASBOURG Cedex, France

<sup>b</sup> IPCMS, UMR 7504, CNRS-Université de Strasbourg, 23 rue du Loess, BP 43, F-67034 STRASBOURG Cedex 2, France

<sup>c</sup> Present address CRPP, Centre de Recherche Paul Pascal, 115 Avenue Schweitzer 33600 PESSAC

† Electronic Supplementary Information (ESI) available: Complete synthesis of  $[3^{2+}][Cl^-]_2$  and  $[3^{2+}][Ag(CN)_2^-]_2$ , DSC measurements and SAXRD for  $[3^{2+}][Cl^-]_2$ . See DOI: 10.1039/b000000x/

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