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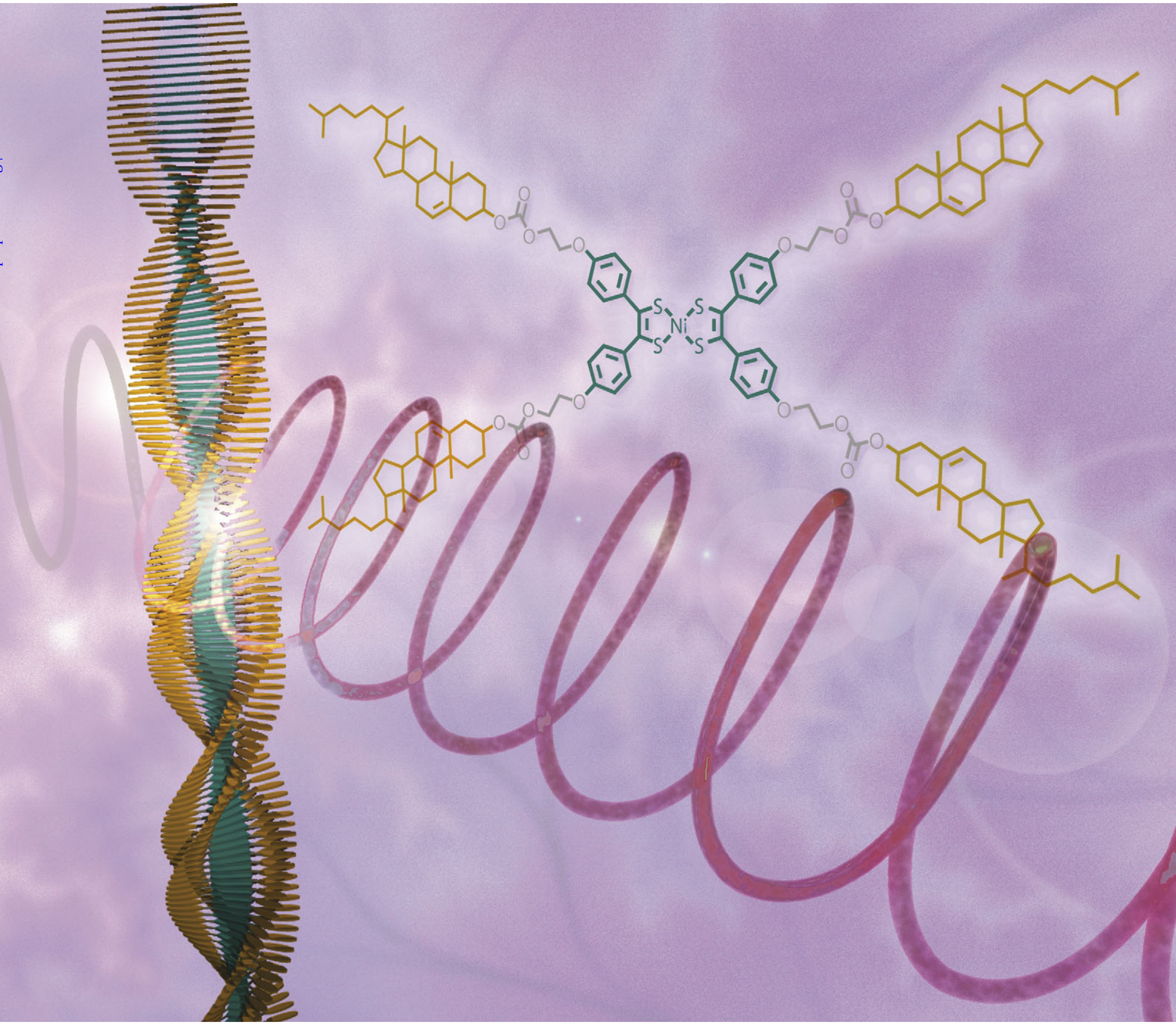

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COMMUNICATION

Near-infrared chiro-optical effects in metallogels†

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A series of novel metallogelators containing near-IR nickel–bis(dithiolene) absorbers were rationally designed and synthesized. Robust gel networks are formed by right handed helical 1D-nanofibers which generate strong and remarkable chiro-optical effects in the near-infrared region.

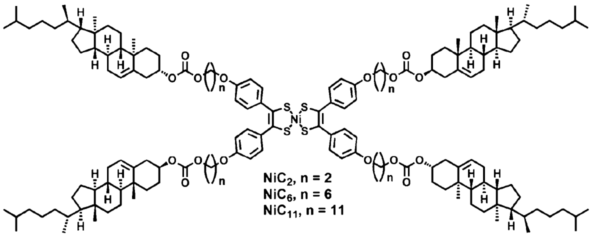
Supramolecular self-assemblies of low-molecular weight gelators is an attractive and elegant way to organize, through spontaneous aggregation, small molecules at the nanoscale level.[1] This gelation phenomenon is generally described as a series of successive supramolecular events, through non-covalent interactions, giving rise to three dimensional architectures, most often consisting of fibrillar networks.[2] Their intriguing supramolecular architectures have potential to pave the way for exotic gel applications such as confined reaction media,[3] templates for well defined inorganic materials,[4] light-harvesting systems,[5] sensors,[6] and biomaterials.[7]

The design of *photoresponsive* gels is particularly appealing for potential applications in various optoelectronic fields.[8] In addition, the dye aggregation inside the self-assembled fibers can allow the tuning and the modulation of the optical properties through the formation of peculiar *J* or *H* aggregates.[9] Furthermore, chiral gelators are also of interest because gelation often leads to helical winding of the fibrils,[10] generating chiro-optical effects when the dye is confined into the chiral architecture. In that respect, cholesteryl fragments are known to be able, when grafted on functional molecules, to produce chiral gels that show dramatic property changes in response to external stimuli, as nicely illustrated in the UV-visible range with oligo(*p*-phenylenevinylene) derivatives.[11] Recently, these chiro-optical effects were extended to the near-infrared (NIR) region after reduction of naphthalene diimine-based gelators, but with low intensity due to the weak absorption of the generated charge-transfer bands.[12] It is all the more unfortunate as NIR chiro-optical effects would be of great interest for potential applications in biological sensing, optical communication and data storage.[2–7]

Metal–bis(dithiolene) and their derivatives are strong NIR absorbers with unique electrochemical properties. They display, in their neutral state, high absorption coefficients (~30 000 M^{-1} cm^{-1}) in a wide range of NIR wavelengths, from 900 nm up to 1600 nm, depending on the judicious choice of metal center and dithiolene substituents.[13] However, despite these exceptional optical properties, no robust and chiral gels based on a metal–bis(dithiolene) core have been yet reported. In addition, gels incorporating metal-chelates (metallogels)[14] display additional unusual functional properties such as redox responsiveness,[15] catalytic action,[16] luminescence properties,[17] spin-crossover phenomena[18] and conductivities[19]. . ..

Herein, we report on the design of novel near-infrared active gelators based on neutral nickel–bis(dithiolene) appended with cholesterol fragments, able to gel solvents and to organize into chiral 1D-nanostructures, displaying strong chiro-optical activity in the near-IR region. Three different complexes, NiC_2, NiC_6 and NiC_{11}, were considered, depending on the length of the spacer between the dithiolene core and cholesteryl fragments (Scheme 1). Experimental details of the synthetic process are presented in the ESI.†

The UV/Vis/NIR absorption spectra of the NiC_n complexes measured in chloroform solution at room temperature display a broad absorption band in the UV range and a strong absorption band is also observed in the near-IR region, centered at 920–930 nm, extending from 700 nm up to 1100 nm, with high extinction coefficients (~30 000 M^{-1} cm^{-1}) (Fig. S1 and Table S1, ESI†). This low-energy absorption band, characteristic of neutral Ni–bis(dithiolene) complexes, is attributed to an electronic transition from the HOMO (Lπ) of b_{1u} symmetry to the LUMO (Lπ*-αd_{xy}) with a metallic character of b_{2g} symmetry.[13] Note that this strong NIR



Scheme 1 Structure of the nickel–bis(dithiolene) complexes NiC_n (n = 2, 6, 11).

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† Electronic supplementary information (ESI) available: Detailed synthetic procedures, cyclic voltammograms, UV/Vis/NIR absorption spectra, gel data, additional AFM pictures and temperature dependent CD spectra. See DOI: 10.1039/c2cc16549j

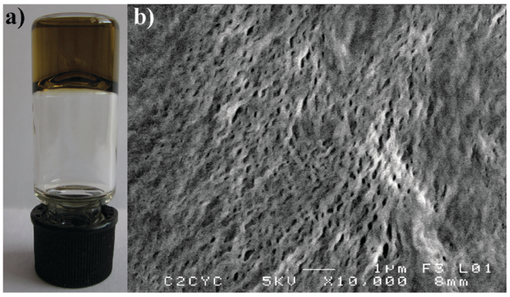

Fig. 1 (a) Gel obtained with complex NiC_2 in dodecane (0.7 mg mL^{-1}). (b) SEM image of a dried gel of complex NiC_2 in cyclohexane (C = 2 mg mL^{-1}).

absorption of the NiC_n complexes arises from the electronic configuration of the Ni–bis(dithiolene) core and is not affected in solution by the presence of the pendant cholesteryl fragments.

Gelation ability of NiC_n compounds (n = 2, 6, 11) has been evaluated in various polar, non-polar, protic, and non-protic solvents (Table S2, ESI†). These compounds are very much soluble in chlorinated solvents such as dichloromethane or chloroform as well as in dioxane or tetrahydrofuran. NiC_2 and NiC_6 complexes displayed excellent gelation abilities in linear alkanes from C_7 to C_{12} carbon chains as well as in cyclohexane at 25 °C, on cooling from warm homogeneous fluid solutions (Fig. 1a). The observed gels are robust, transparent and stable for months; they exhibit thermally-reversible sol to gel phase transitions. NiC_2 was found to be a better gelator with lower minimum gel concentrations (MGC) than NiC_6 while NiC_{11} precipitated from cooled solutions. It appears that longer spacers decrease the gelation abilities of the complexes. We have also synthesized a related complex (NiC_0) in which the cholesteryl fragment is directly linked to the dithiolene by a carbonate function (Scheme S2, ESI†) but this compound was found to be insoluble after heating in linear alkanes. This implies that the introduction of a carbon chain with an optimum length between the metal–bis(dithiolene) core and the cholesteryl fragment is mandatory to favour molecular assemblies in alkanes. Note also that NiC_2 is a supergelator of dodecane with a MGC of only 0.7 mg mL^{-1} (MGC $<$ 1 mg mL^{-1}).

SEM images obtained from a dried gel of NiC_2 complexes in cyclohexane (2 mg mL^{-1}) deposited onto a silicon wafer reveal the presence of a dense 3D network of interlocked twisted fibers with an average diameter of ~100 nm extending over several tens of micrometres (Fig. 1b), responsible for the gelation of solvents. The formation of these twisted fibers is likely due to a helical arrangement of the molecules into 1D assemblies. The width of the fibers is large compared to the dimension of the molecule. Therefore, the observed fibers correspond to bundles of smaller elongated molecular assemblies.

AFM examination of a diluted cyclohexane gel of complex NiC_2 deposited by spin coating on freshly cleaved HOPG confirms the presence of fibrillar assemblies of various sizes (Fig. S2, ESI†). The gels have been diluted five times (diluted gel) with cyclohexane, to disperse the aggregates and hence to facilitate the observation of the individual fibers. The width of the thinnest fiber is 12.0 nm (overestimated in the XY plane by the AFM technique), with a height of 2.60 ± 0.03 nm (Fig. 2).

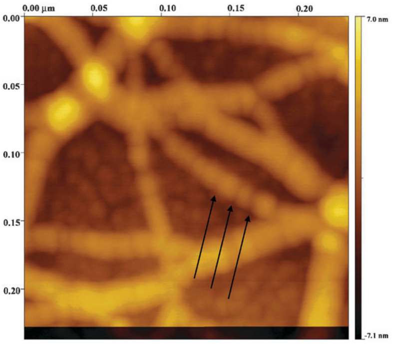

Fig. 2 AFM tapping mode image (0.25 μm × 0.25 μm) of a dried diluted gel of NiC_2 in cyclohexane (C = 0.2 mg mL^{-1}) deposited on HOPG (black arrows show some tilted striations).

These fibers can be considered, in regard to the dimension determined on a Dreiding molecular model (Fig. 3), to be made of a single molecular stack lying flat on the HOPG surface.[16] A closer look also reveals the presence of tilted striations which are assigned to a helical arrangement of the molecules along the stacks (Fig. 2). Similar fibers were observed by AFM with the dodecane gels deposited on silicon (Fig. S3, ESI†). The mean helical pitch measured between two striations is 10.7 ± 0.3 nm. The stacking distance usually observed between metal–bis(dithiolene) cores in columnar mesophases is ~0.35 nm[20] and the one observed between cholesteryl fragments in condensed phase is ~0.5 nm.[21] Note that these stacking distances could not be measured directly by X-ray analysis since XRD patterns of the gels only display broad signals coming from the solvents and the nickel complexes are deprived of mesomorphic properties. Taking these values into account, a stack of ~30 molecules, rotated by 6°, is necessary to complete half of the helical pitch. A possible self-assembly process occurring in cyclohexane gels is presented in Fig. 3. The mismatch between the stacking distance between metal–bis(dithiolene) cores (0.35 nm) and the strong and specific interactions taking place between the cholesteryl fragments at 0.5 nm likely induces the helical stacking of the molecules.

The gel formation appears thus to be a hierarchical process where the complexes first self-assemble into 1D helical stacks, which further intertwine to form twisted bundles, responsible for the immobilization of the solvent. The tilt of the striations, which is identical on all the fibers, indicates that the molecular assembly adopts a right handed (P) helical structure.

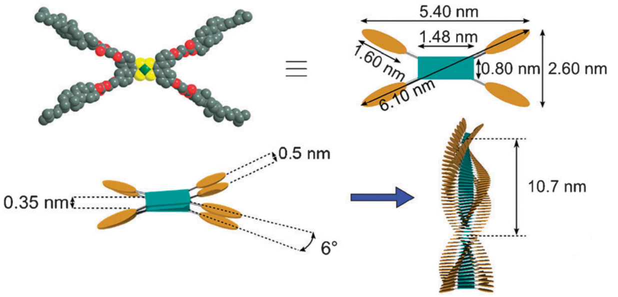

Fig. 3 Schematic representation of the self-assembly of NiC_2 in cyclohexane, taking into account the internal dimensions determined from the AFM experiment.

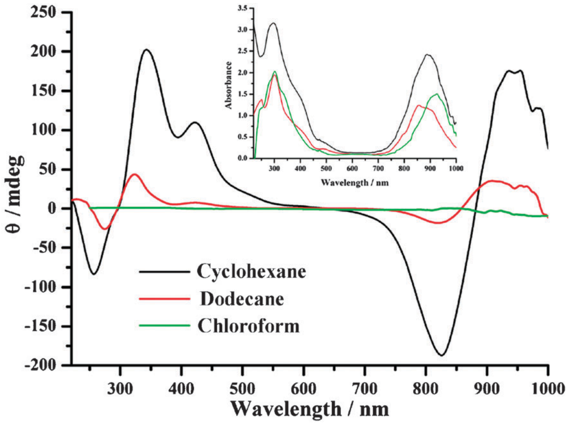

Fig. 4 CD spectra of NiC_2 in chloroform (C = 0.6 mg mL^{-1}) solution and in cyclohexane (C = 1 mg mL^{-1}) and dodecane (C = 0.5 mg mL^{-1}) diluted gels (inset: corresponding UV spectra) (l = 2 mm).

To confirm the sign of the helicity of the molecular assembly, CD measurements have been performed on the gels of NiC_2 complexes, in cyclohexane and in dodecane.

The CD spectra of these two gels show a signal in the UV region with first two positive (λ_{max} = 418 nm and 323 nm) followed by one negative (λ_{max} = 275 nm) Cotton effects. More interestingly, in the near-IR region, we also observe an exciton-coupled bisignate signal with positive (λ_{max} = 945 nm) and negative (λ_{max} = 826 nm) Cotton effects, which changes sign through the HOMO–LUMO absorption maximum at 880 nm (Fig. 4). This behavior is characteristic of a right-handed helical bias of the supramolecular chirality[22] and confirms the AFM observations.

These measurements confirm that the NiC_2 is able to self-assemble in alkanes into right-handed helical fibers and that the formed supramolecular assemblies induce marked chiro-optical effects in the near-infrared region, from 700 nm up to 1100 nm. The anisotropy factor g is higher in cyclohexane gels ($g_{945} = \Delta A_{945}/A_{945} = \theta_{945}/(32\,982 l A_{945}) = 0.015$ with l the cell length in cm and θ in mdeg) than in the dodecane gels ($g_{945} = 7.5 \times 10^{-3}$). Note also that *solutions* of NiC_2 in chloroform were found to be circular-dichroism-inactive (Fig. 4), showing that the simple connection of the chiral cholesteryl fragments on the Ni–bis(dithiolene) core does not allow a direct induction of chiro-optical effects in solution. The self-assembly of the molecules inside the gels into supramolecular helices appears therefore mandatory to generate a CD effect. Indeed, the supramolecular helical organisation allows for an efficient transfer of the chirality from the stereogenic fragment to the center of the fibers which creates a noncentrosymmetric environment around the metal–bis(dithiolene) core. The increase of the temperature, which induces a progressive disaggregation process, leads indeed to a continuous decrease of the CD signal (Fig. S4 and S5, ESI†). Note that the NIR absorption maxima of NiC_2 in cyclohexane and dodecane are not affected by the temperature increase, meaning that the blue shift observed in the gels, compared to the $CHCl_3$ solution (Fig. 4, inset), is essentially due to solvatochromism and not to the formation of H-aggregates in the gel phases.

In conclusion, we have designed and synthesized the very first metal–bis(dithiolene) organogelators (metallogelators), with a characteristic strong NIR absorption, centered at 900 nm in their neutral soluble form, able to form robust chiral gels. In the gel state, the chiral complexes self-assemble into right handed (P) helical supramolecular assemblies, and induce, also in the near-infrared region, efficient chiro-optical effects, from 700 nm up to 1100 nm. Work is under progress to develop also hydrogelators containing such metal complexes strongly absorbing in the near-infrared region, for potential application in the biological window (800–1300 nm).

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