Engineering of an iron–terpyridine complex with supramolecular gels and mesomorphic properties

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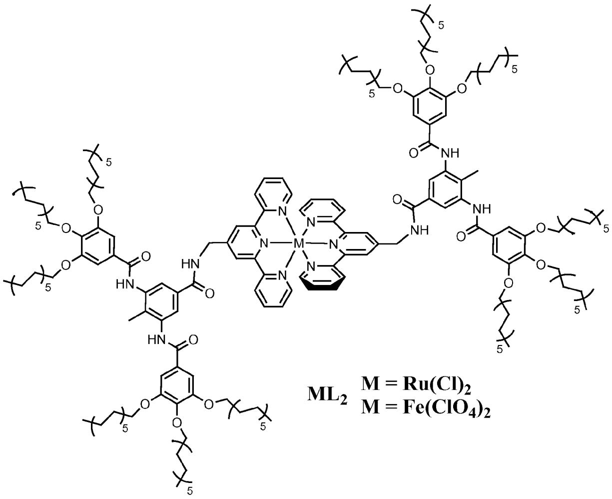
A new iron–terpyridine complex based on a 3,5-diacylamino-toluene platform bearing two phenyl rings appended with aliphatic chains provides robust and transparent organo-gels and liquid-crystalline materials. The LC mesophase was characterized by small-angle X-ray diffraction, and is described as a columnar phase with a rectangular lattice symmetry. Based on the measured parameters, a molecular packing model is suggested in which two complexes aggregate together to form a pseudo elliptical plateau; the latter then pile up to form the columns.

A challenging research area in modern chemistry is the design and synthesis of multifunctional compounds and soft materials with desirable or predictable properties such as luminescence, transport of information, catalytic activity, nano-structuration and macroscopic ordering.[1,2] For this purpose, a steady and progressive interest is devoted to the synthesis of oligopyridines and an impressive number of such functional molecules have already been designed. Oligopyridine compounds exhibit interesting synthetic facets and some of them were found to show important antibiotic and fungicidal character. Moreover, they form stable complexes with many cations. We recently argued the case that balancing the rigid core of phenanthroline–copper complexes with flexible appendages allowed the production of organogels and mesophases over a large temperature range.[3]

Along these lines 2,2′:6′,2″-terpyridine (terpy) ligands appeared to be particularly attractive.[4] The resulting complexes have many potential applications in macromolecular science, biochemistry, photophysics, and nanoscience. In particular, terpy and its multiple derivatives have advantageously been used as building blocks for the engineering of spiral lines,[5] dendrimers,[6] micelles,[7] polymers,[8,9] and liquid crystalline materials.[10] Formation of ordered architectures on surfaces[11–13] and functional molecular devices for single-atom transistors[14] are particularly challenging. Recently, biochemical applications were reported describing the potential use of terpy-complexes as sensors in medical research and as polypeptide binding agents.[15] Ruthenium–terpy complexes have received much attention in the field of energy suppliers such as solar cells,[16] and luminescence devices.[1b,17] Immobilization of terpy ligands and complexes on polymer resins could prove to be of importance in the field of molecular catalysis.[18]

Although system-containing terpy offer an enormous structural diversity and tunability in terms of potential properties, stability and processability, examples of terpy based organogelators or mesomorphic ligands and complexes are scarce. Up to now, only dinuclear copper(I) metallo-mesogens involving segmented and bulky terpy ligands appeared to behave as liquid crystalline materials,[19] thus contrasting with the non-mesomorphic uncomplexed ligand. Recent studies have described terpy-containing carboxylic acids that form hydrogels, in which the three-dimensional network is provided by electrostatic interactions induced by proton transfer from the acidic to the basic nitrogen atoms of the terpy ligand.[20]

In the present letter, the design of terpy chelates tethered to a central 3,5-diacylaminotoluene platform equipped with two lateral aromatic rings each bearing three appended aliphatic chains is presented. This new ligand allows both organogels and mesomorphic materials stabilized by extended hydrogen bonded networks to be obtained. It is also demonstrated that the complexation of this functional molecule to iron(II) cation allows the production of original metallo-organogelators and metallo–mesogens.



Ligand **L** was prepared by a convergent strategy adapted from the already reported preparation of phenanthroline based 4-methyl-3,5-diacylamidophenyl platforms.[21] After purification, ligand **L** was obtained as a sticky and soft material and the observation of a birefringent texture by polarized optical microscopy points to its mesomorphic state.

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The methyl group bisecting the central phenyl was introduced to force the amide vectors to point out of the plane and to extend the dimensionality of the hydrogen bonded network. Ligand **L** displays a FT-IR spectrum consistent with hydrogen bonding through the amide groups: ν_{NH} at 3320 cm^{-1}, ν_{CO} at 1660 cm^{-1} and δ_{NH} 1517 cm^{-1} (in the solid state).[22] The Ru-complex was prepared by reacting two equivalents of **L** with $[Ru(DMSO)_4Cl_2]$[23] in refluxing chloroform. The resulting orange-red complex was isolated as the chloride salt by column chromatography, with ν_{NH} at 3368 cm^{-1} (ν_{NH}), at 1651cm^{-1} (ν_{CO}) and at 1526 cm^{-1} (δ_{NH}), and (ES-MS: *m*/*z* 3583.2 $[M - Cl]^+$ and 1774.2 $[M - 2Cl]^{2+}$). The Fe-complex was directly obtained by mixing stoechiometric amounts of the ligand with $Fe(ClO_4)_2 \cdot 6H_2O$ under anaerobic conditions. This complex exhibits a molecular peak at 3601.1 $[M - ClO_4]^+$ and 1751.2 $[M - 2ClO_4]^{2+}$ in the ES-MS and a solid state FT-IR spectrum with bands located at 3273 cm^{-1} (ν_{NH}, very large), at 1660 and 1644 cm^{-1} (ν_{CO}) and at 1520 cm^{-1} (δ_{NH}), showing the presence of two different types of hydrogen bonds involving the amide functions.

The gelation abilities of the free ligand and associated metal complexes were tested by heating a cyclohexane solution and then cooling to room-temperature. **L** forms a colorless and transparent organogel (Fig. 1a) which is stable over a long time (at least during a six months time-scale period).

Interestingly, the Fe-complex also provides a transparent highly colored gel in cyclohexane (Fig. 1b) with a minimum gelation concentration (MGC) of 3% (w/w), whereas its Ru-analogue did not lead to a gel under the same conditions (Fig. 1c). For both complexes the color is imported by the presence of a strong metal-to-ligand charge transfer state expected by the presence of the terpyridine ligands $\lambda_{max} = 479$ nm for Ru with $\varepsilon = 15\,000$ M^{-1} cm^{-1} and $\lambda_{max} = 555$ nm for Fe with $\varepsilon = 7900$ M^{-1} cm^{-1}. The organogels exhibited thermally reversible sol–gel transitions and the FT-IR spectra revealed that the amide groups are involved in a tight hydrogen bonding network ν_{NH} at 3279 cm^{-1}, ν_{CO} at 1641 and 1662 cm^{-1} and δ_{NH} 1519 cm^{-1} (in the L-gel), and ν_{NH} at 3317 cm^{-1}, ν_{CO} at 1662 and 1643 cm^{-1} and δ_{NH} at 1519 cm^{-1} (in the Fe-gel). It is likely that this supramolecular network is responsible for the formation of fibers which aggregate in a 3D network of interlocked fibers leading to the gelation of cyclohexane (Fig. 2).[3,24]

From a general point of view it is well-known that iron(II) salts have a very high affinity for terpyridine ligands and indeed such chelates are widely used to determine infinitesimal amounts of iron salts in analytical tests.[25] As a consequence, one interesting aspect of the nanostucturation of **L** would be to understand the consequence of iron salt diffusion in the **L**-gel. Doping the **L**-gel by a solution of cyclohexane–THF (10%) containing around 0.1 equiv. of Fe(II), does not break the gel but the characteristic violet color of the complex readily developed in the viscous solution (Fig. 1d). In marked contrast when iron dust is sprayed over the **L**-gel, the progressive formation of the complex (over one week, Fig. 3), irreversibly destroys the gel, probably due to the presence of excess salts. Previous studies have shown that the presence of transition metal ions has a pronounced effect on the gelation ability of ligands whereas in some cases the formation of the gel is completely suppressed.[26] It is noteworthy to observe the formation of the complex under these conditions due to the very low solubility of the salt in cyclohexane.

The ability of **L** and its corresponding Fe-complex to form robust and transparent gels made of fibers prompted us to study their liquid-crystalline properties by heating the solvent-free materials.

The thermotropic behavior of **L** was studied by interplaying thermogravimetric analyses (TGA), differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction. **L** is liquid crystalline from room temperature up to 225 °C, the temperature at which a reversible transition

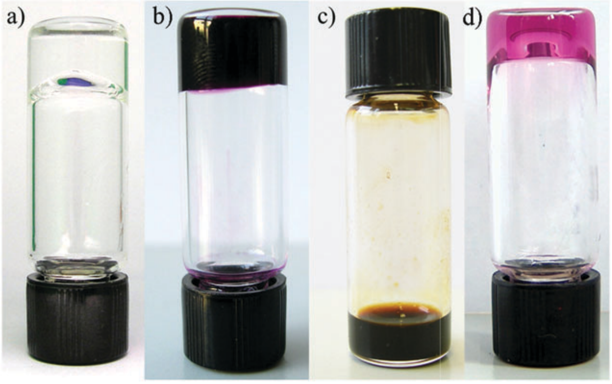

Fig. 1 a) Gelation test in cyclohexane of **L** in cyclohexane (2.6% (w/w)); b) Gel obtained with the complex $[FeL_2](ClO_4)_2$ in cyclohexane at a concentration of 3.1% (w/w) after heating and cooling cycle; c) Solution of the ruthenium complex $[RuL_2](Cl)_2$ in cyclohexane (C = 3.3% (w/w)); d) **L**-gel doped with *ca.* 0.1 equiv. of Fe(II). 0.1 mL of a solution of cyclohexane–THF (10%) containing 0.1 equiv. of $Fe(ClO_4)_2$ was deposited on the **L**-gel in cyclohexane–THF (10%) (6.1% (w/w; 10 mg in 0.2 mL of cyclohexane–THF (10%) mixture). Gel formation is confirmed when the sample does not flow once the test tube is turned upside-down.

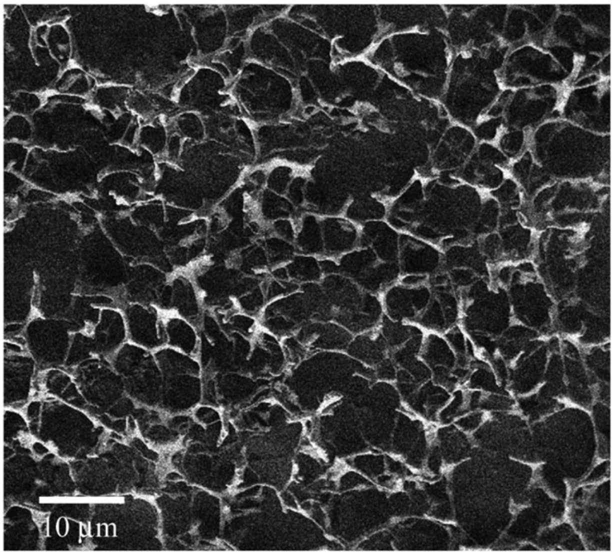

Fig. 2 SEM picture of freeze dried gel of the Fe–terpy gel from cyclohexane showing formation of interlocked and elongated objects (C = 3.2% (w/w)).

Fig. 3 Solution obtained when $Fe(ClO_4)_2$ dust is sprayed over a **L**-gel (3.3% (w/w)) after 3 days (b), after 5 days (c) and after 7 days (c). The salt dust is visible in the bottom of the flask.

is detected on both heating and cooling by DSC ($\Delta H = 21.8$ J g^{-1}). An X-ray diffraction pattern registered at 120 °C unambiguously confirms that the compound is liquid crystalline (Fig. 4a). The broad halo A at *ca.* 4.6 Å corresponds to the average distance between the molten chains. Two slightly less diffuse halos B and C were observed at 7.25 and 3.8 Å, respectively and were attributed to some liquid-like (short-range) correlations between neighboring molecules. Three reflections, a sharp and intense peak followed by two less intense higher orders, are observed in the small angle region and indicate the long-range positional ordering of large objects. The small-angle reflections could be indexed as the fundamental 001, and two harmonics 002 and 003 reflections of a lamellar phase ($d = 26.1$ Å at 120 °C). Above 225 °C, this compound is in the isotropic liquid state.

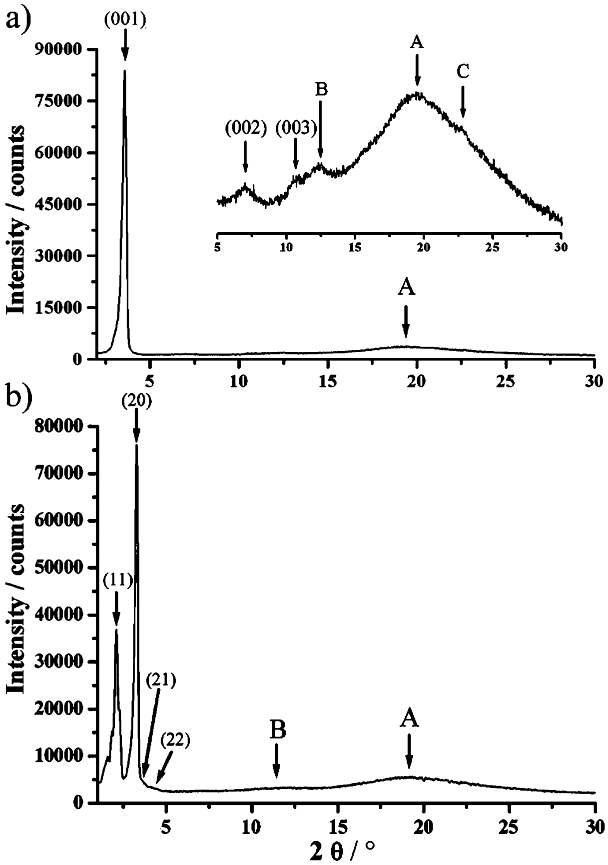

Fig. 4 a) XRD pattern of **L** at 120 °C; b) XRD pattern of the Fe complex at 150 °C.

The Fe-complex decomposes above 180 °C as observed by TGA analysis. No phase transition was detected by DSC measurements from the ambient up to the degradation temperature. Observations under polarized optical microscope reveal a birefringent soft and malleable material which is a good indication of its liquid-crystalline behavior. No recognizable texture could be observed, partly due to the impossibility to reach the isotropic liquid, and thus to grow natural texture free of paramorphotic defects. In order to elucidate the molecular organization of these mesostructured materials, a series of temperature-dependent wide and small-angle X-ray scattering (WAXS, SAXS) measurements on powder samples were performed. An X-ray pattern obtained at 150 °C displayed in the wide angle regime a diffuse and broad scattering-halo A centered at 4.6 Å, indicative of a liquid-like order of the aliphatic chains and thus of the fluid-like nature of the phase (Fig. 4b). Another diffuse scattering halo associated to a distance of 7.5 Å (halo B), is also observed and was attributed to some short-range stacking of the molecules. In the small-angle region, the XRD pattern displayed four reflections which can be indexed in the *p2gg* rectangular symmetry as $(hk) = (11), (20), (21), (22)$ with lattice parameters $a = 51.5$ and $b = 69.6$ Å ($S = a.b = 2 \times S_{col} = 3584.4$ Å^2) at 150 °C. X-ray patterns obtained at various temperatures between the ambient and 180 °C are totally consistent with a rectangular columnar mesophase stable from room temperature to 180 °C. Quite remarkably the structurally related Ru complex is devoid of mesomorphic behaviour. The absence of gels and liquid crystal properties for the $[Ru(\mathbf{L})_2]Cl_2$ complex might be related to the nature of the counter-anion. The effects of the counter-anions in ionic metallomesogens[2b] have been investigated in detail by several research groups but their influences on the mesomorphic properties cannot be simply rationalized, and still remain highly speculative.[2b] It is admitted that perchlorate anions are hydrogen bond acceptors and could be engaged in multiple hydrogen bonds with NH groups,[27] contrasting with the behaviour of the chloride ions. Thus, the presence here of perchlorate ions in the Fe-complex might help in giving structure to the soft material by rigidifying and reinforcing the cohesion of the molecular architecture.

In order to get some insight of the packing of the Fe-complexes inside the columns and of the 2D arrangement of the latter in the rectangular lattice, a standard geometrical

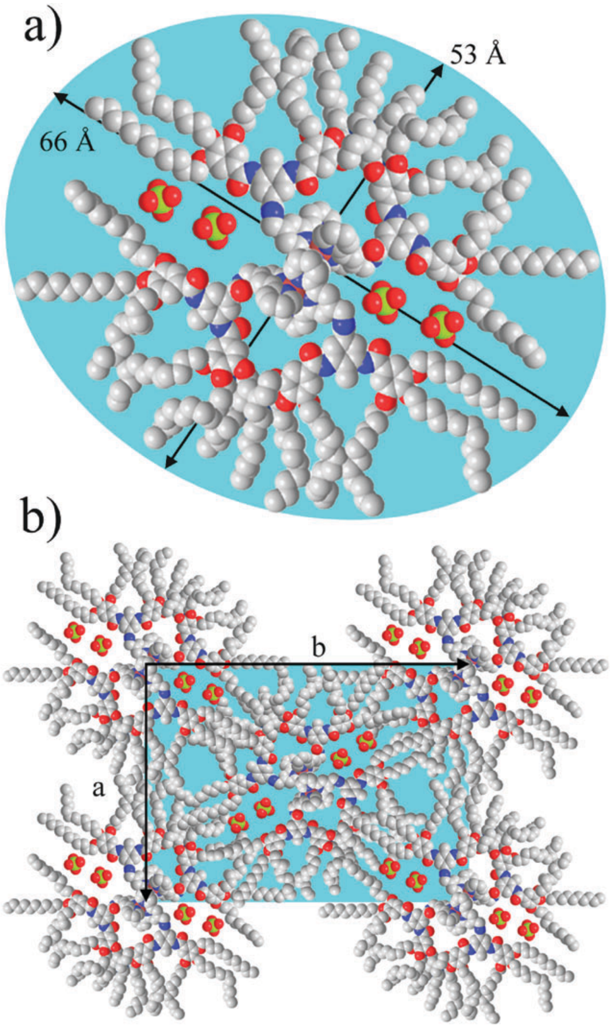

Fig. 5 a) CPK model of the Fe complexes in a V-shape conformation and their arrangement in a dimer to form the elementary plateau. b) Illustration of the good space filling of the rectangular unit cell with lattice parameters $a = 51.5$ and $b = 69.6$ Å.

treatment was applied.[28] Thus, the packing may be characterized by two structural parameters:[29] the columnar cross-section, S_{col}, and the stacking periodicity h along the columnar axis, both parameters being analytically linked through the $hS_{\mathrm{col}} = NV_{\mathrm{m}}$ relation, where N is the number of molecules within a columnar stratum h-thick and V_{m} is the molecular volume. Considering a density close to 1 (*ca.* 0.9 at 150 °C), the molecular volume was found to be about $V_{\mathrm{m}} = 6725$ Å^3. Taking $h = 7.5$ Å as the columnar stratum thickness (and corresponding to the halo B), an exact value of two is obtained for N, indicating that there are two molecular equivalents of the Fe complex per such defined plateau. With these additional data in hand, a CPK model was constructed, as illustrated in Fig. 5, which allows for a good description of the space filling of the rectangular mesophase unit cell. The counter-anions are arbitrarily located in the unoccupied volumes created by this molecular arrangement. The complexes likely adopt a V-shape in order to introduce interactions between the terpyridine fragments facilitating their aggregation into pseudo dimers. To compensate for the width of the complex, greater than the height of the stratum ($w > h$), an axially shifted packing of these dimeric species may be envisaged. In this way, an optimal micro-segregation between the aliphatic parts and the polar parts inside a plateau is ensured, which is not achievable in the case of linear conformation of the complex.

The main interest in this class of compounds stems from its facile synthesis and ready substitution. A vast range of derivatives and complexes could be anticipated with properties tuned to particular applications. In short, **L** is representative of a new class of organo-gelator and liquid crystalline ligand able to chelate a variety of different metals. The molecular dimensions of these molecules and their attributes are such that they are able to make gels with solvents. At this point, diffusion of iron in ligand gels is feasible to some extent but detrimental at high concentration. The emergent metallomesogen has many features of merit due to its stability over a large range of temperature and to the possibility to import properties of the coordinated metal such as anisotropy, polarisability, photo- and electroactivity and magnetic features. The testing of these supramolecular soft materials in electro-optics and photonics is currently in progress.

Experimental

Syntheses

Ligand L. A Schlenk flask equipped with a septum and an argon inlet was charged with 3,5-bis(3,4,5-tridodecyloxybenzoylamino)-4-methyl benzoic acid (0.35 g, 1.1 equiv., 0.23 mmol) dimethylaminopyridine (DMAP) (0.06 g, 2.2 equiv., 0.47 mmol) in anhydrous CH_2Cl_2 (50 mL). The mixture was stirred until complete solubilisation of the acid. 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI) (0.09 g, 2.2 equiv., 0.47 mmol) and 4′-aminomethyl-2,2′;6′2″-terpyridine (0.06 g, 1 equiv., 0.21 mmol) were added to the clear solution and stirred overnight. After evaporation of the solvent, purification was performed by flash chromatography on silica gel with CH_2Cl_2/MeOH (99.9/0.1 to 98/2) and followed by crystallisation from CH_2Cl_2/CH_3CN (0.200 g, 56%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.89 (t, $^3J = 4.5$ Hz, 18H, CH_3), 1.26 (m, 108 H, CH_2), 1.72 (m, 12H, CH_2), 2.21 (s, 3H, CH_3), 3.95 (m, 12H, OCH_2), 4.40 (d, $^3J = 3.96$ Hz, 2H, CH_2), 7.20 (m, 6H, H arom.), 7.66 (td, $^3J = 7.7$ Hz, $^4J = 1.7$, 2H, CH), 7.90 (s, 2H, CH), 8.01 (s, 2H, CH), 8.26 (d, $^3J = 7.9$ Hz, 2H, CH), 8.49 (d, $^3J = 4.3$ Hz, 2H, CH), 8.65 (s, 3H, NH). IR (KBr): 3437, 3271, 2923, 2853, 1640, 1584, 1521, 1494, 1468, 1426, 1406, 1384, 1334, 1263, 1232, 1115 cm^{-1}. MS (FAB$^+$, *m*NBA): m/z (%) = 1724.2 (100) $[M + H]^+$. Anal. Calcd (%) for $C_{110}H_{174}N_6O_9$: C, 76.61; H, 10.17; N, 4.87; Found (%): C, 76.52; H, 10.04; N, 4.75.

$[Ru(L)_2](Cl)_2$. Ligand **L** (0.066 g, 0.038 mmol) and Ru(DMSO)$_4$Cl$_2$ (0.013 g, 0.026 mmol) were heated at 80 °C during 6 h in a mixture of $CHCl_3$ (10 mL) and EtOH (10 mL). During the course of the reaction the color turned progressively brown. The complex was isolated by column chromatography on silica using a gradient of methanol (1 to 10%) in dichloromethane. The deep orange complex was recrystallized by slow evaporation of dichloromethane from dichloromethane–

acetonitrile mixture (0.060 g, 87%). IR (KBr): 3369, 2923, 2853, 1719, 1651, 1582, 1526, 1494, 1465, 1434, 1378, 1334, 1222, 1114 cm^{-1}. Anal. Calcd (%) for $C_{220}H_{348}N_{12}O_{18}RuCl_2$: C, 72.97; H, 9.69; N, 4.64; Found (%): C, 72.39; H, 9.31; N, 4.29.

$[Fe(L)_2](ClO_4)_2$. To an argon degassed dichloromethane solution (20 mL) of ligand **L** (0.082 g, 0.047 mmol), a degassed methanol solution (5 mL) containing $Fe(ClO_4)_2 \cdot 6H_2O$ (0.009 g, 0.026 mmol) was progressively added and the solution turned instantaneously deep-violet. The complex was isolated by slow evaporation of dichloromethane from dichloromethane–acetonitrile mixture (0.080 g, 92%). IR (KBr): 3273, 2922, 2853, 1660, 1645, 1583, 1526, 1520, 1495, 1469, 1456, 1427, 1379, 1335, 1230, 1114 cm^{-1}. Anal. Calcd (%) for $C_{220}H_{348}N_{12}O_{18}FeCl_2O_8$: C, 71.34; H, 9.47; N, 4.54; Found (%): C, 70.86; H, 9.03; N, 4.25.

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