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A. Agosti, E. Kuna, G. Bergamini, "*Divergent terpyridine-based coordination for the construction of photoactive supramolecular structures*", *Eu. J. Inorg. Chem.*, **2019**, 577-584.

Which has been published in final form at:

<https://onlinelibrary.wiley.com/doi/full/10.1002/ejic.201801263>

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1 **Supramolecular Architectures****Divergent Terpyridine-Based Coordination for the Construction of Photoactive Supramolecular Structures**Amedeo Agosti,^[a] Ewelina Kuna,^[a] and Giacomo Bergamini*^[a]

Abstract: Exploring new materials to manipulate luminescent radiation and investigate the interaction of light and matter is one of the most compelling prospects of our century. Supramolecular chemistry has unraveled the opportunity to synergistically combine the chemical and optoelectronic properties of the most diverse classes of compounds. Among these, terpyridines have acted as pivotal ligand units that enable self-assembly of multicomponent chromophoric systems. In this review we therefore elucidate the metal-coordinating ability of

these materials, that promote a plethora of aggregation-induced phenomena. In particular, fluorescence tuning, reversible stimuli-responsive phosphorescence enhancement and low-dimensional complexation have been demonstrated for carbon and sulfur based terpyridine oligomeric structures. Common thread of such processes is the versatile application of light as a trigger for spectroscopic investigation and output for superior optical, medical and sensing devices.

1. Introduction

The first publication concerning the chemistry of terpyridine compounds appeared at the beginning of the 1930s, when Morgan and Brustall described the synthesis of 2,6-bis(2-pyridyl)pyridine (Tpy).^[1,2] It was then demonstrated how this tridentate ligand could create highly stable complexes by chelating a wide range of transition metal ions in their low oxidation states, due to strong metal-ligand (d- π^*) back donation.^[3] From that moment on, terpyridine has been considered as a suitable building block for supramolecular construction, being extremely versatile in terms of functionalization at every ring-position through various substitutions or interconversion reactions.^[4] Over time, terpyridines and their functionalized analogues have been gaining ground on the field of supramolecular and coordination chemistry, as well as material science, mainly due to their ability to create stable complexes with appealing optical, electronic, and magnetic properties.^[5-8]

Interestingly, terpyridine metal complexes $[M(\text{Tpy})_2]^{n+}$ usually possess a distorted octahedral coordination geometry, caused by hexacoordinate metal ions,^[9] where a linear bilateral conformation of ligands can be obtained by complexation of terpyridine ligands to a metal center in 2:1 ratio.^[10] The directionality of these non-covalent bonds is crucial in the design and construction of supramolecular systems, either presenting flexible and rigid polymer-like conformation or geometrically well-defined architectures.

The formation of tailored self-assemblies can be provided by a suitable terpyridine construction strategy, where the coordi-

nation process and structural configuration of the metal-ligand complexes might be affected by the rigidity of the self-assembled system.^[11] Terpyridines moieties can be linked via a rigid spacer, forming a predictable structure, or by flexible units, yielding a random architecture.^[12,13] The possibility to combine various bridging ligands drives different physics and geometry of self-assembling multinuclear complexes, offering diverse supramolecular architectures including grids and racks,^[14] macrocycles^[15] or metal coordination polymers^[16] (Figure 1).

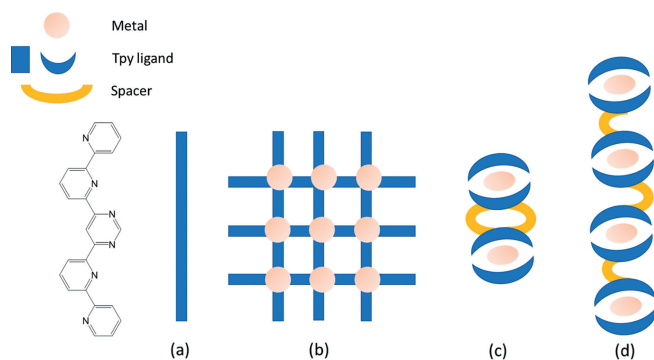


Figure 1. Schematic representation of a mononuclear (a) racks, (b) grids, (c) macrocycles, and (d) linear metallopolymer.

Likewise, the ligand-metal-ligand connectivity allows to control bond strength and, ultimately, design the supramolecular self-assemblies architecture.^[13] Being the formation of terpyridine-based structures driven by the interplay between kinetics and thermodynamics driving forces, Tpy ligands can coordinate both labile (Cd^{2+} ; Zn^{2+}) and non-labile (Fe^{2+} ; Os^{2+} ; Ru^{2+}) metals, with increasing complexation kinetic rates in the order ($\text{Cd}^{2+} < \text{Zn}^{2+} < \text{Fe}^{2+} < \text{Os}^{2+} < \text{Ru}^{2+}$).^[17]

As a consequence of the high binding affinity, custom-made terpyridine monomers combined with suitable metals give rise

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to programmable and highly ordered 2D^[18–20] and 3D structures.^[21–23] These supramolecular materials based on terpyridine-containing p-conjugated polymers found application in optoelectronic devices like organic light-emitting diode,^[24] photovoltaic cells,^[25] organic field-effect transistors^[26] and ion sensors.^[27,28] Beyond this, the design of reversible and flexible metallo-polymeric systems allows the integration of such architectures even in biological environments (e.g. as biological marker).^[29]

Another key feature of terpyridine-based materials is related to their photophysical properties. Pristine Tpy shows an absorption spectrum below 300 nm and weak emission ($\Phi_{em} = 0.003$) around 330 nm. The successive protonation of the pyridinic nitrogen provides significant changes in both the absorption and emission spectra, boosting the fluorescence quantum yield above 70 % ($\Phi_{emTpyH^+} = 0.17$ and $\Phi_{emTpy2H2^+} = 0.71$).^[30] In the same way, metal ion complexation causes strong redshifts in the absorption spectra, along with changes in the emission properties, depending on the metal ion involved. Moreover, chemical functionalization of Tpy allows fine tuning of the optical and electronic properties of the ligand and metal complexes. For instance, in order to improve the optical properties and move the absorption and emission spectra to the visible region, the conjugation system of the terpyridine moieties can be extended by attaching appropriate substituents, especially in the 4' position of terpyridine units.^[9] The use of 4'-substituted ligands allows to obtain a linear vector between the two para substitution groups (Figure 2), providing higher control on the energy and electron transfer through ligand-ligand, ligand-metal or metal-ligand interactions.^[31]

An explanatory example is the case of the $Ru(Tpy)_2^{2+}$. In contrast to bipyridine complexes, ruthenium terpyridine complexes

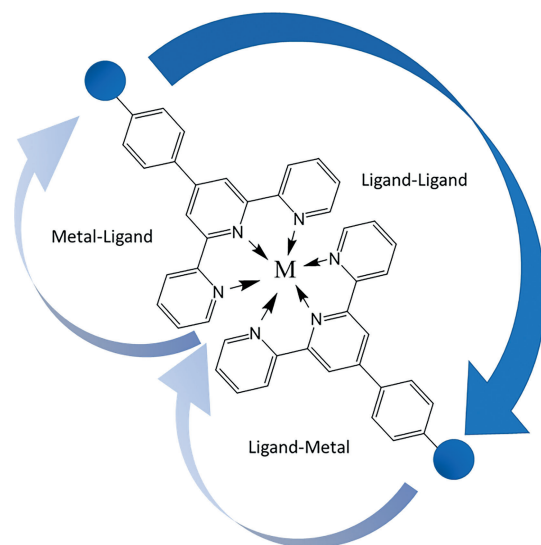
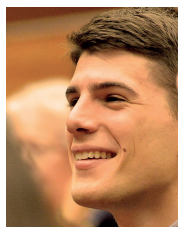


Figure 2. The potential pathway of the energy and electron transfer in 4'-substituted terpyridine dyads complex.

do not emit at room temperature due to a non-radiative transition of the excited triplet metal to ligand charge-transfer state (3MLCT) via a triplet metal centered state (3MC) to the ground state.^[32] However, through incorporation of an electron withdrawing or donating group, the energy band gap between triplet states can be widened, improving the photophysical behavior.^[6] Hence, the various functionalized terpyridine ligands allow to fine-tune the optical properties of the parent mononuclear complexes (dyads or triads) and extended supramolecular frameworks (i.e. polynuclear complexes). In order to enhance the photophysical properties, a variety of chromophores have been appended to the Tpy moiety, thus combining lumines-



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cence and photoinduced energy and/or electron transfer processes with metal binding properties.^[5,31]

Finally, the peculiar photophysical properties and responsivity to external stimuli make terpyridines a perfect tool to monitor self-assembly, metal coordination and photoinduced processes. Experimental investigation of absorption changes, emission or lifetime quenching and sensitized emission, can indeed provide information on the stoichiometric ratio, interaction among the different units inside the supramolecular architecture and, ultimately, on the effect of the environment.

This minireview therefore aims at summarizing a set of experimental contributions from our research group, in which terpyridines have been used as binding sites in the construction of 2D and 3D supramolecular structures with intriguing photophysical properties.

2. C-Based Multiterpyridine Systems

The most common method to obtain highly luminescent terpyridine molecules is extending the rigidity and π -conjugation of the system by functionalization of the phenyl-ring in the 4' position of Tpy units (so called Kröhnke-type terpyridine).^[6] Although the nonplanarity between phenyl and terpyridyl rings reduces electron delocalization, 4'-*p*-tolyl-2,2':6',2''-terpyridine (hereafter called TolTpy) exhibits improved luminescence features in the UV spectral region with 8 % emission quantum yield in organic solvents. Hence, in this section, we report the divergent functionalization of a sp^3 carbon and a benzene with multiple TolTpy units, which, upon addition of specific metal ions, self-assemble in nanostructures.

2.1 Tetrahedral Shaped

A first example of C-based multiterpyridines is represented by a tetrahedral core functionalized with four Tpy units (TTT; Figure 3).

The sp^3 core conveys a tetrahedral symmetry to the rigid molecule, spatially segregating the Tpy moieties and thus pre-

venting intramolecular 2:1 Tpy:Mn⁺ complexation. Exploiting the strong chelating activity of the Tpy binding pocket, the complexation of TTT with Fe²⁺ and Ln³⁺ ions was investigated with the aim of determining the stoichiometry, stability and photophysical properties of the formed species. The addition of 151 Fe(CF₃SO₃)₂ to a diluted solution of TTT in dichloromethane generates significant changes in the absorption spectra, namely a bathochromic shift of the Tpy absorption band at 300 nm, characterized by an isosbestic point at 328 nm, associated with the appearance of a MLCT band at 575 nm. The corresponding 156 emission spectra, obtained through excitation at the isosbestic point, showed strong quenching of the fluorescence band at 380 nm. Analysis of the UV/Vis traces variation shows a titration plateau when 2.0 eqs of Fe²⁺ with respect to TTT were added to the solution, or at half eq. of Fe²⁺ for each terpyridine unit. 161 Consequently, the metal to ligand charge transfer (MLCT) band for Fe-TTT complex showed 4-fold increase in the molar absorptivity, compared to the simple [Fe(Tpy)₂]²⁺ complex.^[33] From these results, we can assume that all the terpyridine units present in TTT molecules are engaged in metal complexation 166 with 2:1 Fe/TTT stoichiometry. Moreover, it was noticed that the emission intensity, detected via excitation at the isosbestic point, is not superimposed on that of the absorption decrease at 300 nm. Following the addition of 1 eq. of Fe²⁺, absorption settles indeed to 50 %, while the emission intensity of TTT li- 171 gand decreases to 10 %, likely suggesting an interaction, occurring in the excited state, between free and complexed Tpy units. This hypothesis was corroborated by nanosecond lifetime investigation of the excited state, together with the use of low concentration of TTT, which ruled out the intervention of inter- 176 molecular interactions. Furthermore, taking into consideration the stoichiometry and the fact that no precipitation was observed, we speculated the formation of nanometer-sized assemblies. The resulting oligomeric structure, probed by Dynamic Light Scattering (DLS) and Atomic Force Microscopy (AFM), consists indeed of particles of approximately 20 nm diameter. Finally, aggregation of these nanoparticles gradually leads to formation of "polymer" chains (up to 5 μ m long) that are stable

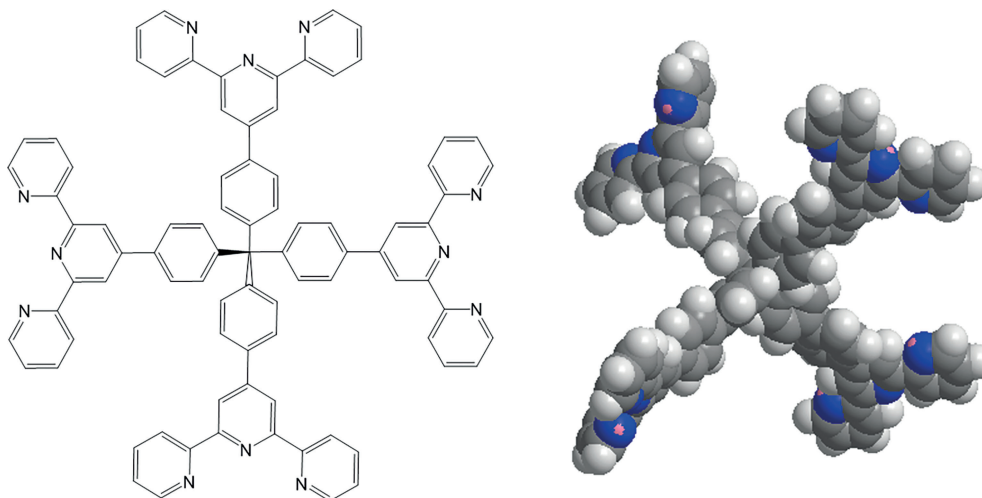


Figure 3. 2D and 3D structure of TTT ligands.^[33]

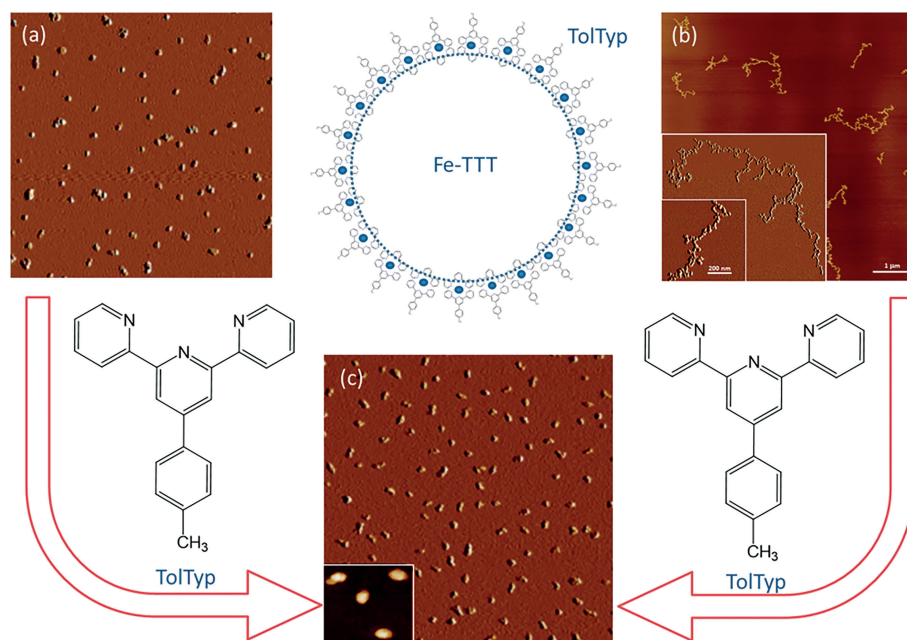


Figure 4. AFM images of (a) Fe-TTT particles; (b) polymeric chain of aggregates; (c) individual particle after the addition capping agent (TolTpy).

for weeks without further precipitation. The “polymerization” process is triggered by the presence of the free metal coordination sites located on the nanoparticles surface, providing quasi-fractal structures peculiar to diffusion-controlled aggregations.^[33]

Interestingly, aggregation proceeds along discrete axes, maintaining the original particles within the assembly, and does not occur via formation of globular particulate entities. Further analyses are required to provide a comprehensive description of the process mechanism, however it is safe to propose that aggregation does not proceed randomly, nor depends on concentration. Remarkably, polymerization may eventually be halted by the addition of TolTpy units as a capping agent, allowing self-assembly control from molecular up to mesoscopic scale (Figure 4).

Subsequently, the investigation of TTT molecule optical and chemical properties addressed the self-assembly behavior in relation to luminescence properties of TTT-Mn⁺ (Mn⁺ = Zn²⁺, Eu³⁺, Nd³⁺, Yb³⁺).^[34] First of all, we confirmed the formation of 2:1 Mn⁺:TTT complexes, monitoring the changes in the absorption and emission spectra, as well as stable assemblies around 50 nm in size (by DLS and AFM measurements). Of particularly interest is the emission intensity evolution, characterized by the complete quenching of the TTT emission and concomitant increase in the Zn²⁺, Eu³⁺, Nd³⁺ and Yb³⁺ complexes emission, spanning from the visible to the near infrared (NIR) region (Figure 5).

The addition of TolTpy as capping agent to the particles, not only improved the stability and prevented further polymerization, but also improved the emission properties of the Eu³⁺-TTT and Nd³⁺-TTT nanostructures. The complexation of two different luminescent metal ions by TTT ligands results in the formation of dual emissive particles. Notably, the addition of 0.2 equivalents [Nd(CF₃SO₃)₃] to a solution of TTT·2Eu^{III} decreased

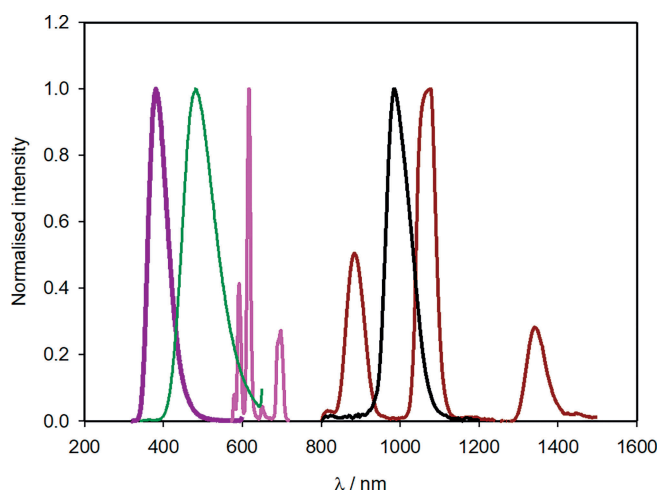


Figure 5. Normalized emission spectra of TTT (purple line), TTT·2ZnII (green line), TTT·2EuIII (violet line), TTT·2NdIII (brown line) and TTT·2YbIII (black line) in CH₂Cl₂.^[34]

the Eu³⁺ emission by 64 % and the associated emission of the Nd³⁺ ion in the NIR region. Analysis of the quenching and sensitization rates confirmed that such process is not a mere displacement of Eu³⁺ ions by Nd³⁺ ions, otherwise a decrease of Eu³⁺ phosphorescence of 20 % should have been observed. DLS and AFM measurements confirmed the presence of 50 nm particles and therefore the unchanged size or arrangement of the oligomeric structures. Hence, the possibility of combining different metal centers allows to design heterometallic multinuclear complexes with multiple emission.

2.2 Planar Shaped

The functionality of TolTpy unit was also investigated when attached to a benzene core, resulting in a rigid and planar struc-

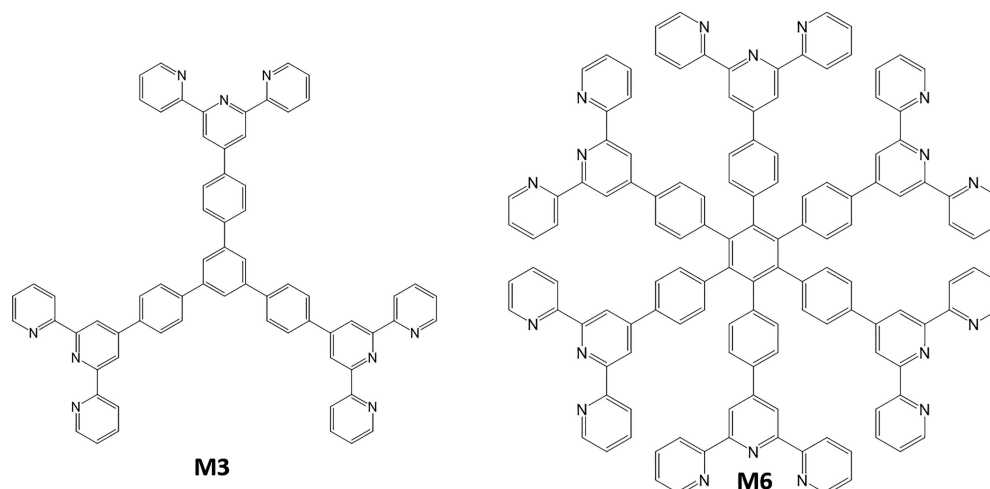


Figure 6. Chemical structure of M3 and M6 multiterpyridine ligands.

ture with superior luminescence properties ($\Phi_{em} \approx 35\%$), containing 3 and 6 binding sites (hereafter called M3 and M6) (Figure 6). To this extent, M6 molecules were previously employed in the construction, at air-liquid interfaces, of free-standing 236 monolayer sheets grasped together by metal ions.^[35,36]

In particular, our research group contributed to the study of the behavior of M3 and M6 as multiterpyridine ligands for Zn^{2+} and Fe^{2+} ions in dichloromethane solution. At first, we demonstrated the formation of 2:1 Tpy: M^{2+} complexes, for both metal 241 ions and in a low concentration regime, which eventually produced a polymeric structure characterized by multiple ligands organized in coordinative bonds. Later, a detailed analysis of the proposed polymer-like compound and its spatial arrangement was performed by modelling of the speculated structure.

As previously described, monitoring of the optical absorption features allowed the observation, for M^{2+} and M6, of single metal ion bonded to two Tpy units belonging to distinct ligands. In this case, the plateau was reached upon the addition of 3 eqs of M^{2+} per M6 unit, thus at half eq. of metal ions per 251 Tpy moiety. Finally, by integrating the photophysical results with computational modelling of the 2D and 3D structures, it was possible to infer that, with reference to previous studies conducted at the air-water interface, a predominant 2D grid is formed in solution (Figure 7), nonetheless the final structure 256 probably resulted in a folded configuration. Remarkably, our

findings reveal that the concentration of 3D defects, despite being present, was evaluated to be rather negligible compared to the overall metal to ligand ratio.

Overall, these results shed new light on the formation of 2D metal-coordinated polymers and will hopefully trigger a body 261 of research in the application of such materials in the field of molecular sieves, ultrasensitive pressure-sensors, and surface coatings.^[8]

3. ArS-Based Multiterpyridine Systems

In this section we report the description of two examples of 266 multiterpyridine systems based on two particular organic luminophores: hexathiobenzene^[37] and tetrathioapyrene,^[38] which are attractive candidates for applications like organic light-emitting diodes, field-effect transistors, liquid crystals, and many other solid-state devices. 271

3.1 Hexathiobenzene

Firstly, we synthesized a multichromophoric supramolecular system characterized by six phenylterpyridine units attached through a sulfur atom to a benzene core (BzSTpy, Figure 8). The core of our molecule, more specifically a hexathiobenzene 276 molecule decorated with six tolyl groups, exhibits outstanding phosphorescence properties both in the solid state (Φ_{em} ca. 100% and $\tau = 4$ ms)^[37] and when dispersed in a matrix at 77–110 K, but does not reveal any luminescence in liquid solution at room temperature. The emission “onset” was justified accord- 281 ing to intramolecular rotations restriction, a behavior also known as Aggregation Induced Emission (AIE). This atypical emission can be observed either in the solid state or in extremely diluted matrices at sufficiently low temperature (77–110 K), both scenarios being characterized by a rigid cage-like 286 environment with limited intramolecular rotations. Therefore, we proposed the integration of terpyridine ligands in a multi-component chromophore (BzSTpy Figure 8) with the aim of boosting the luminescence properties of the aforementioned compound. Upon addition of appropriate divalent metal ions 291

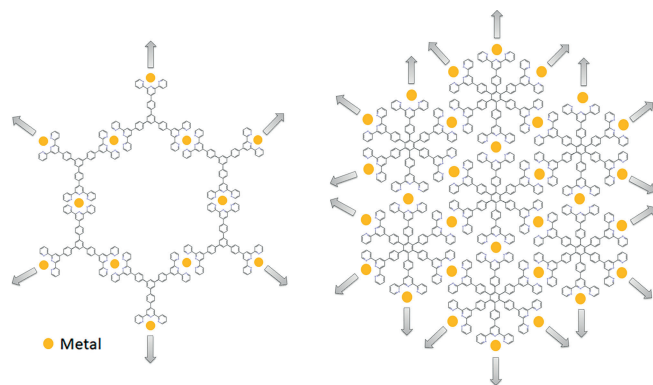


Figure 7. Schematic representation of a 2D structure formed by M3 and M6.

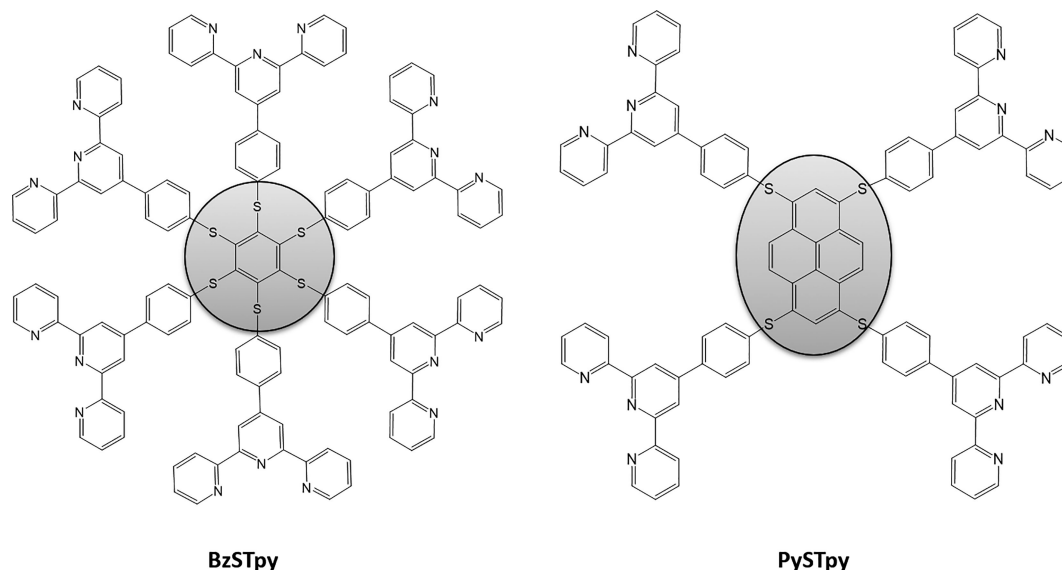


Figure 8. Chemical structure of BzSTpy and PySTpy.

to a solution of BzSTpy, a supramolecular polymer with a 3:1 Mn^+/X stoichiometry is formed. Particularly interesting is the case of Mg^{2+} ions, which self-assemble into a bright ($\Phi_{em} = 10\%$) phosphorescent supramolecular polymer, with microsecond-excited state lifetime in air-equilibrated THF solution. Remarkably, the spectral trace of the compound in solution perfectly matches that of the powder, corroborating the formation of an aggregated coordination compound with reduced intramolecular rotations and motions, thus enhanced phosphorescence. In addition to that, upon excitation of the $[Mg(Tpy)_2]^{2+}$ units of the polymeric structure, sensitization of the core phosphorescence takes place with $> 90\%$ efficiency. Moreover, by addition of Fe^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} no phosphorescence was detected, because of the expected photoinduced energy/electron transfer processes between the phosphorescent core and

the low energy excited states of the metal complexes at the periphery. Nevertheless, these phenomena are not favored in presence of Ca^{2+} , Zn^{2+} , and Cd^{2+} , which are d^0 or d^{10} metal ions, yielding instead a phosphorescence band observed for Mg^{2+} with significantly reduced efficiency. Ultimately, we also reported the reversible complexation behavior of the BzSTpy- Mg^{2+} structure when tetrabutylammonium fluoride was added to the liquid solution. Altogether, the BzSTpy compound benefits from ion complexation not only in the formation of a luminescent supramolecular polymer, but also from the reversible assembly of such structure, opening its utilization as a light-responsive sensor for both anion and cation (Figure 9).

3.2 Tetrathiopyrene

Another example of ArS-based multiterpyridine concerned the investigation of the compound composed by four terpyridine units connected to a tetra(phenylthio)pyrene core (PySTpy, Figure 8). The superior photophysical and electrochemical properties of 1,3,6,8-tetrasubstituted pyrene core, together with its specific geometry, indeed contributed to its wide use in several technological fields^[39] and resulted to be highly desirable also for our investigation purposes. The optical features of tetra(*p*-tolylthio)pyrene can be easily identified in the absorption spectrum between 380 and 470 nm,^[40] while TolTpy produces the band at 295 nm. These distinct spectral signatures evidence the lack of significant pyrene/terpyridine ground-state interaction; as a result of this PySTpy can be safely considered a supramolecular specie. On the other hand, the emission spectra, distinctly obtained by selective excitation of Tpy (UV region) and Pyrene (visible region) moieties, are identical and show an intense fluorescence band with a maximum at 460 nm ($\Phi_{em} = 51\%$ and $\tau = 1.2$ ns) attributable at the tetra(*p*-tolylthio)pyrene core. Owing to the fact that no TolTpy emission was detected and considering the perfect overlap between excitation ($\lambda_{em} = 460$ nm) and absorption spectrum of PySTpy, it was inferred

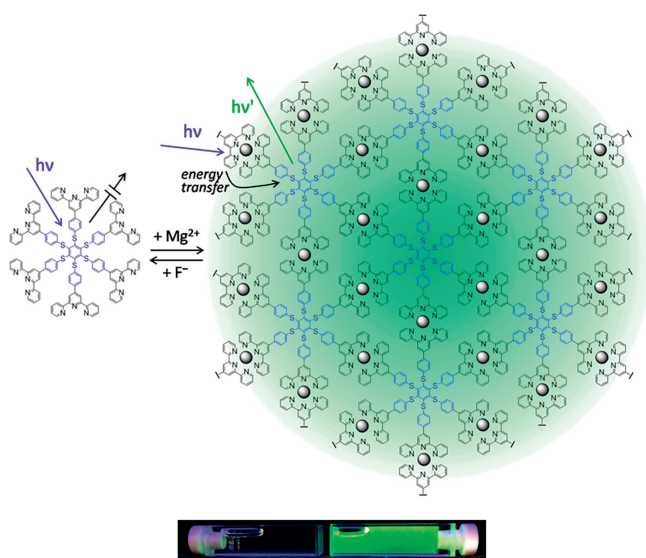


Figure 9. Schematic representation of the supramolecular polymer and the energy transfer process involved. Bottom: pictures of the monomeric and polymeric solutions.

341 that intramolecular energy transfer not only occurs with unitary efficiency, but also with specific directionality, namely from peripheral chromophores to the core.

Next, metal ion complexes formation was observed via addition of Fe^{2+} , Zn^{2+} , and Nd^{3+} salts in diluted solutions. In particular, an intermolecular 2:1 Tpy: M^{n+} complex organizes, thanks to the divergent geometry and specific stoichiometry, in a "super" oligomeric structures built on $[\text{M}(\text{Tpy})_2]^{n+}$ interactions. DLS and AFM experiments further defined such stable nanoparticles to possess hydrodynamic diameters between 50 and 80 nm, depending on the metal ion employed. Interesting results have been obtained through investigation of the photoinduced processes in the final metal-coordinated supramolecular structure.

As already stated, all the metals employed form nanometric structures and the emission of the core is completely quenched after the addition of 2 eqs of metal ions. This behavior can be ascribed to photoinduced energy and/or electron transfer process from the pyrene excited state and the metal complex formed. In the case of Fe^{2+} , the presence of fast non-radiative decay channel, characteristic of the lowest energy MLCT excited state of the pristine $[\text{Fe}(\text{Tpy})_2]^{2+}$ complex, determines the expected fluorescence intensity quenching. On the other hand, the interaction between Zn^{2+} and PySTpy is characterized by a concomitant decrease of the band of the core at 460 nm and rise of a very weak Zn-Tpy emission band at 540 nm. The measurements of the excitation spectrum, fixing $\lambda_{\text{em}} = 540$ nm, perfectly matches the absorption spectrum, confirming the occurrence of directional energy transfer from the outer to the inner region of the Zn-PySTpy system.

Finally, similar results have been obtained in the case of Nd^{3+} , where the addition of 2 eqs of the Ln ion causes complete quenching of the core emission and boosts sensitized emission of the Nd^{3+} ions in the NIR region. Also in this case, core to metal complexes energy transfer with unitary efficiency has been measured.

To sum up, in the present study we demonstrated that the addition of different metals ions not only controls the formation

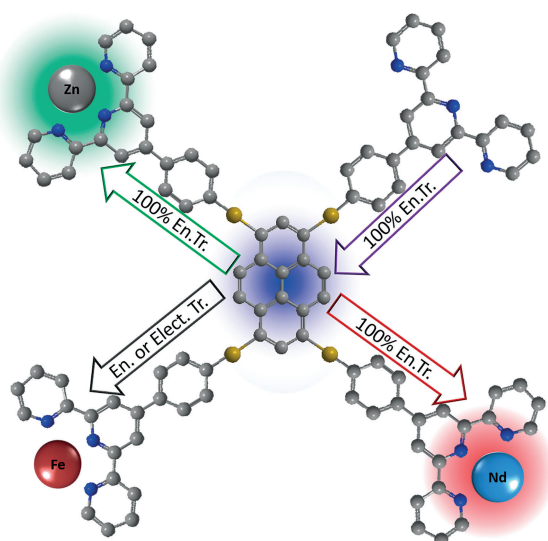


Figure 10. Schematic representation of the intramolecular energy and/or electron transfer processes.

of three-dimensional nanoscopic objects, but also switches the direction of the intramolecular energy transfer (Figure 10) in a dual function.

4. Conclusion

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This review has endeavored to highlight the exceptional versatility of the 2,2':6',2''-terpyridine metal-binding domain in coordination chemistry. This class of molecular ligands has been widely investigated owing to their ability to form highly stable complexes following d-block metal ion coordination, featuring unprecedented optoelectronic, magnetic, and electrochemical properties. In particular, we aimed to raise attention on the role of light-matter interaction for this class of compounds. The generation of light by fluorescence or phosphorescence are powerful resources extensively used in the fields of medicine, environmental chemistry, sensing, and several others. Furthermore, under a more fundamental point of view, luminescence signals enable extremely sensitive investigation of dendritic structures and superstructures. Therefore, the present review has highlighted the capitalization of light both as a tool for fundamental research and as an output enabling cutting-edge optical technologies.

At first, fluorescence modulation was demonstrated for the family of terpyridines including carbon-based units. Emission from these chromophores can indeed be tuned from the visible to the NIR and, by judicious choice of the metal ions, even simultaneously occurs in dual regions thanks to distinct multinuclear complexation sites. Surprisingly, oligomer formation of such structures retained the morphology of the primitive unit, proceeding along discrete axes and without globular particulate development. A similar remarkable assembly behavior was described for multi-Tpy ligand systems branching out of a benzene core. Specifically, the supramolecular architectures ensuing from complexation arise in the form of a reticulated monolayer, having metal ions as net points, as neatly confirmed by absorption spectroscopic studies. In addition to that, depending on the nature of the metal used, the structure can undergo transmetalation processes, both in random or directed fashion, still retaining the polymeric integrity.

Finally, our research group benefited from terpyridine compounds in the construction of light-harvesting antenna systems and highly luminescent supramolecular polymers. In the former case, a supramolecular, metal coordinated, polymer structure based on a tetrathiophene core revealed 100 % efficient directional energy transfer from the periphery to the central units. This process occurs thanks to $[\text{M}(\text{Tpy})_2]^{n+}$ interactions and was demonstrated for an arsenal of metal ions, namely Fe^{2+} , Zn^{2+} , Nd^{3+} , enabling broad fluorescence tuning. Additionally, metal ion coordination allowed sensing features when Tpy units were appended to sulfurated benzene core compounds. Through the reversible formation of a polymeric antenna, phosphorescence was indeed turned on and off thanks to the AIE effect.

To conclude, the research just described should highlight the phenomenal adaptability of the terpyridine unit to a host of chromophoric structures, boosting their structural and optoelectronic properties in fluid solution. We also envisage an in-

crease in the use of light as a powerful tool to critically investigate supramolecular compounds and their application to a broad range of energy and medical applications.

436 Acknowledgments

We gratefully acknowledge the H2020-MSCA-ITN-2016 (722591-PHOTOTRAIN).

Keywords: Terpyridine · Supramolecular chemistry · Luminescence · Polymers

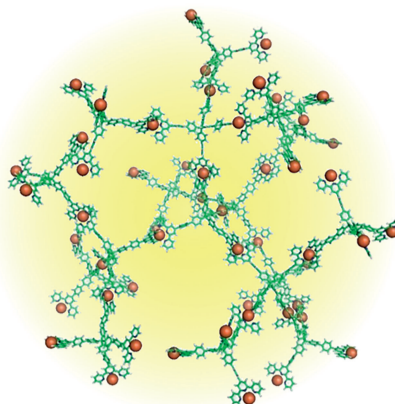
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Received: October 15, 2018

Supramolecular Architectures

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531 Divergent Terpyridine-Based Coordination for the Construction of Photoactive Supramolecular Structures



Terpyridine is one of the most intriguing building blocks in the construction of photoactive supramolecular architectures, and light is the perfect tool to investigate their structure and to exploit optical and electronic functions.

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DOI: 10.1002/ejic.201801263