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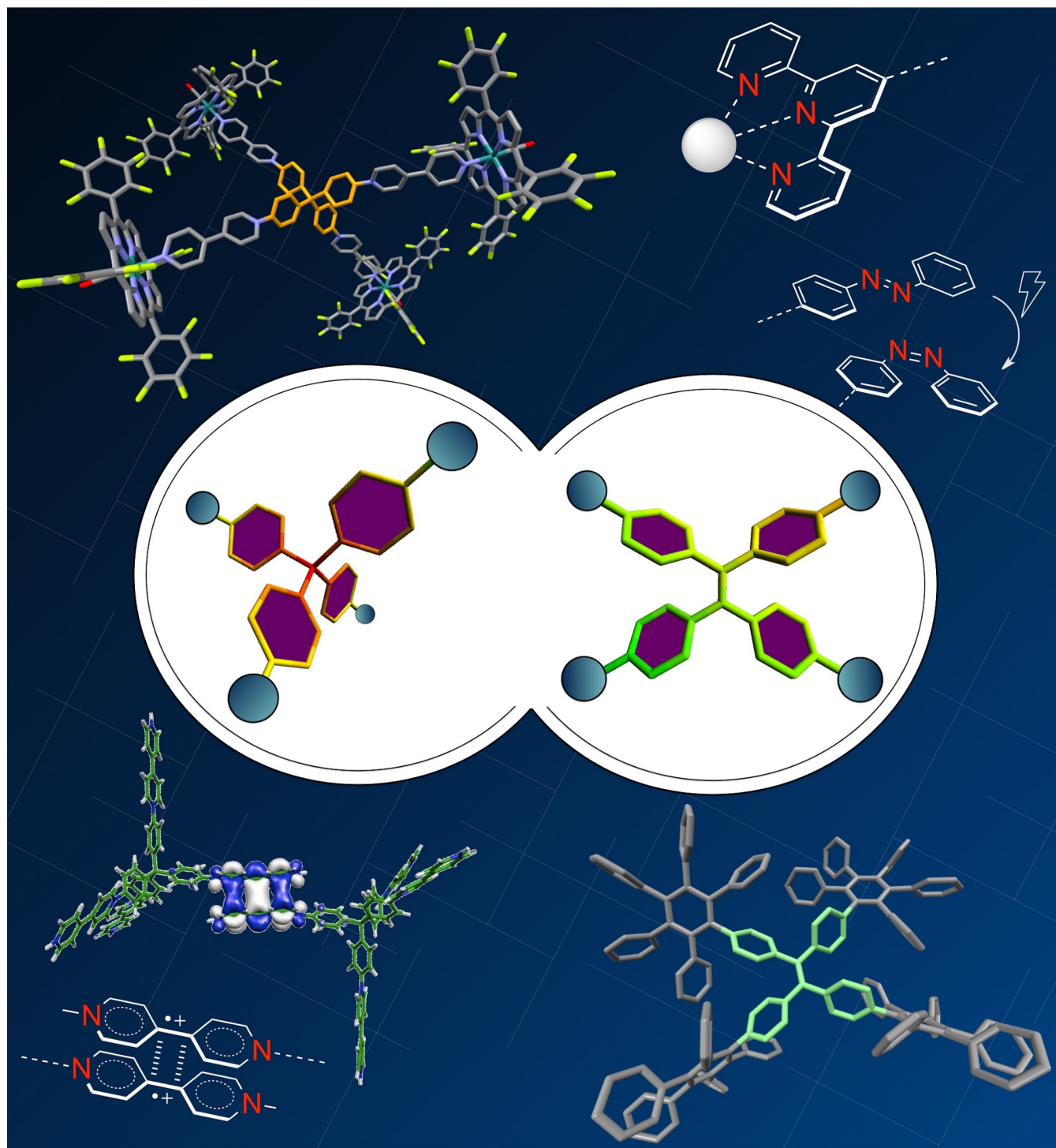Societies Publishing

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Tetrachromophoric Systems Based On Rigid Tetraphenylmethane (TPM) and Tetraphenylethylene (TPE) Scaffolds

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Tetraphenylmethane (TPM) and tetraphenylethylene (TPE) are among the most common rigid molecular architectures able to spatially arrange four peripheral functional groups. The aim of this Review is to provide a thorough description of the properties that supramolecular systems consisting of four chromophores (common supramolecular motifs, ligands, redox centers and conventional luminophores such as polypyridyl ligands, viologens, and azobenzene units) attached to TPM and TPE cores can show. Specifically, the photophysical properties of these molecules as well as the electronic interactions of the chromophores either in the ground or in the excited states will be highlighted and discussed, outlining the relationship among cores and outer subunits.

1. Introduction

Multichromophoric systems feature multiple chromophores confined in a nanometer-sized space and, in most of them, electronic interactions among chromophores occur either in the dark (ground state level) or upon light stimulation (electronically excited states).

In Nature, multichromophoric systems span from light-harvesting pigment-protein complexes to nucleic acids. The former work as light-harvesting antennae by collecting excitation energy from the sun and funneling it to the reaction center where charge separation occurs, while the latter are designed to dissipate the absorbed energy as quickly as possible to prevent photodamages. Nowadays, they are the object of intense study by ultrafast and two-dimensional spectroscopic techniques and by computational analysis to model their photoinduced activity.[1]

Artificial multichromophoric systems are frequently inspired by biosystems and feature a variety of scaffolds: polymers, dendrimers[2] (i.e. well-defined macromolecules exhibiting a tree-like architecture), zeolites (e.g., zeolites L are crystalline aluminosilicates in which one-dimensional channels can encapsulate dyes in an organised architecture), nanoparticles functionalised at their surfaces with chromophores or containing them encapsulated within their structure. They have been employed not only as light-harvesting antennae,[3,4] but also as sensors with signal amplification,[5,6] sensitization of photovoltaics,[7,8] and bioimaging.[9]

Rigid multichromophoric systems constitute an appealing subset,[10] in which the shape-persistent architecture enables an accurate control of the distance among the chromophores and a fine tuning of their electronic interactions. Within this complex and diverse field, the present review will focus on tetrachromophoric systems based on two rigid scaffolds, namely tetraphenylmethane (TPM) and tetraphenylethylene (TPE, see Figure 1), which can retain precise spatial arrangements of the attached peripheral groups despite the presence of phenyl rings on the core, that are able to rotate freely.

TPM has tetrahedral shape and is innocent from the electronic point of view: the lowest-energy absorption band and fluorescence band ($\lambda_{max} = 272$ and 332 nm in DMSO, respectively) are located at very high energy,[11,12] compared to the most common chromophores. On the other hand, tetraphenylethylene is a chromophoric scaffold with an ethylene core featuring a planar geometry and four geometrically strained phenyl subunits: it absorbs at ca. 310 nm in THF and exhibits Aggregation Induced Emission (AIE) in the visible spectrum ($\lambda_{max} = $ ca. 450 nm),[13] as reported by Tang and coworkers in the noughties.[14,15] The term AIE refers to the fact that the molecule is not luminescent in fluid solution but becomes fluorescent in aggregated state, e.g. in solid phase or colloidal dispersions. Therefore, the presence of chromophores appended at its periphery can in principle modulate its AIE activity as well.

The present minireview will discuss the photophysical properties of these supramolecular systems and the electronic interactions among them and with the rigid scaffold. The choice of examples was based not only on the intrinsic interest of the topic itself, but also on the availability of systems featuring the same chromophores with both scaffolds for a comparative purpose.

Other multifunctional scaffolds are represented by adamantane,[16] tetraphenylsilane,[17] spiro compounds,[5] arenes,[18–20] porphyrins,[21] and phthalocyanines,[22] among others: interested readers can refer to the related literature reports for a more comprehensive discussion and detailed analyses.
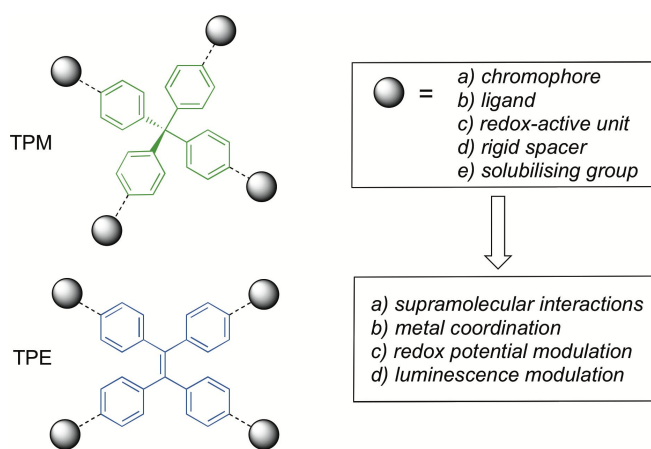
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Figure 1. Schematic representation of the TPM and TPE derivatives and their potential applications in multichromophoric systems.

2. Tetraphenylmethane (TPM) derivatives

Tetraphenylmethane is a simple polyaromatic molecule where a central carbon atom is substituted with four phenyl groups. Thanks to the sp³ hybridization of the carbon, the structure is tetrahedral. The central carbon atom not only creates the tridimensional structure but also drastically reduces the conjugation between the phenyl rings, as observed by the absorption and emission spectra in the UV-blue region.

The functionalization of the phenyl ring of TPM leads to the incorporation of different functional groups like halides,[23] alkenes,[24] carboxylic acids,[25] amines[26] or alcohols.[27] The introduction of these functional groups opens this molecule to further improve the design of the structure to take advantage of the rigid and tetrahedral structure of the core.

Thanks to a rigid branched architecture, TPM finds application in supramolecular chemistry as stopper or pseudo-stopper like in catenanes,[28] molecular machines,[29] and as tetragonal node in metal organic frameworks (MOFs).[17]

In the following sections we will focus on supramolecular systems based on TPM functionalized with four chromophoric groups (Figure 2). We will focus on the effect of the rigid scaffold, the occurrence of new properties, and the interaction of each unit with its neighbors.

2.1. Terpyridine derivatives

Polypyridyl units have found several applications in supramolecular chemistry as powerful and versatile ligands.[30–33] The tetrahedral structure of TPM has an ideal geometry to create 3D structures by coordination of terpyridine units with metal ions. For example, a shape-persistent tetra-terpyridyl ligand based on TPM (**TPM-Tpy**, Figure 3a)[34] is
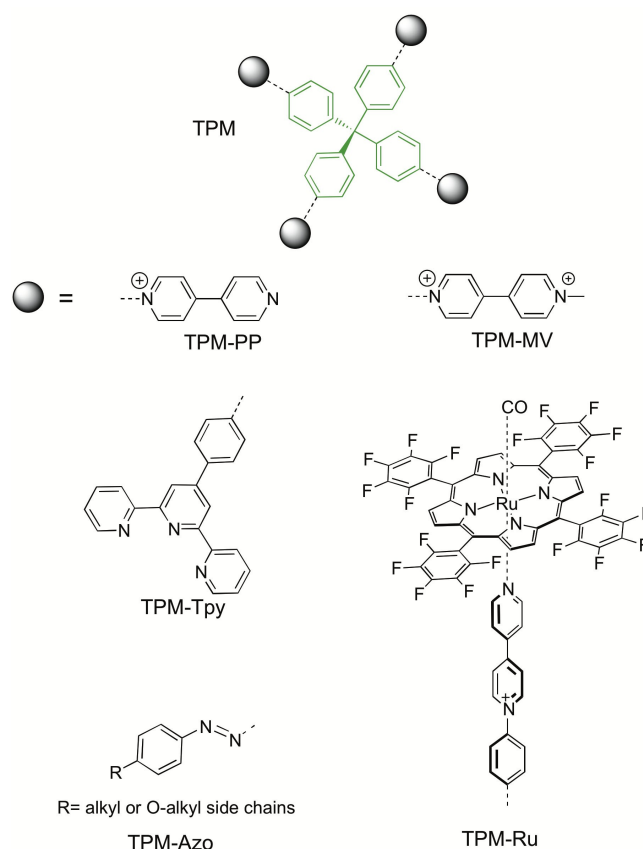
Figure 2. Schematic representation of the TPM derivatives discussed.

able to coordinate transition metal ions, leading to a three-dimensional self-assembled structure. The self-assembly process occurring at the molecular level (nanoscale) drives the

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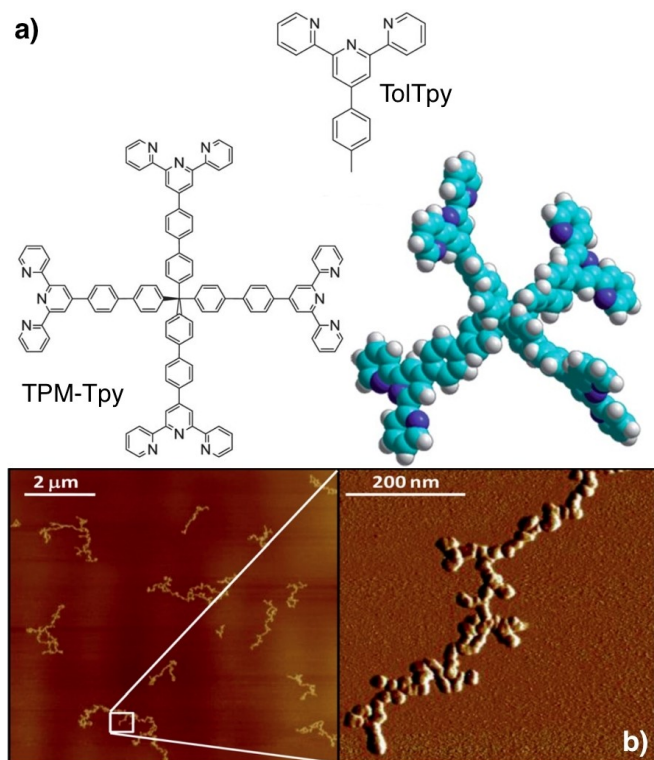
a)

Figure 3. a) Chemical structure of **TPM-Tpy**, model compound **TolTpy**, and 3D optimised model of **TPM-Tpy**. b) AFM images of a **TPM-Tpy** solution containing 2 eq. of Fe^{2+} and spin-coated on mica 16 h after its preparation. Peak force image (left) and zoomed area of the same image demonstrate the formation of individual particles (right). Reproduced with permission (Ref. [34]). Copyright 2017, Royal Society of Chemistry.

formation of mesoscopic objects at the microscale. The design of the compound allowed to allocate four spatially segregated terpyridyl moieties linked to a central TPM to obtain a tetrahedral symmetry. **TPM-Tpy** shows a high absorptivity in the near-UV region and an intense fluorescence in the visible spectrum. Compared to plain terpyridine (**TolTpy**), both the lower energy absorption and the emission bands are red-shifted, due to the increased degree of conjugation. The intramolecular 1:2 (metal:ligand) complexation is prevented by the rigid tetrahedral structure of the molecule: it follows that **TPM-Tpy** ligands are held together by complexation to Fe^{2+} ions, thereby building up a supramolecular polymer structure in which each Fe^{2+} ion is surrounded by two terpyridyl units residing on two different **TPM-Tpy** molecules. This complexation yields to nanoparticles of hundreds of nanometers size that could form polymeric fiber chains with dimensions up to the macroscale (5 mm in length), that can be observed by AFM measurements and that show high stability for weeks without further precipitation (Figure 3b).

2.2. Azobenzene derivatives

Azobenzene is a photochromic compound that undergoes E→Z photoisomerization with a drastic change in the polarity and in

its spatial arrangement[35] and is one of the most popular photochromic molecules. A TPM scaffold was functionalized with four azobenzene units[36,37] by azocoupling with tetraamino-TPM (Figure 4). All four azobenzene moieties undergo E→Z photoisomerization with UV light (365 nm) both in solution and in solid state, with the concomitant shift to higher energy and intensity decrease of the π-π* band ($\lambda_{abs} = 345$ nm). Upon near-UV (330–380 nm) irradiation of the crystals, its morphology changes (Figure 4c–d) and the optical birefringence disappears consequently. The crystals appear therefore to melt, and the material assumes the features of a viscous liquid.

Interestingly, during irradiation of **TPM-Azo(C16)**, small changes in the positions of the isosbestic points detected in the absorption spectra are observed and a decrease in the E→Z photoisomerization quantum yield is also determined. These two observations point out that the four azobenzene units exhibit similar but not identical photophysical and photochemical properties. The authors also observed[37] that the tetrahedral structure effectively promotes a clean and reversible photochromism in the solid state, and that the introduction of electron donating groups in the outer phenyl ring of the azobenzene units increases the degree of photoconversion compared to similar compounds displaying alkyl peripheral substituents.[36] In turn, no relevant differences are detected in the composition of the photostationary state as a function of
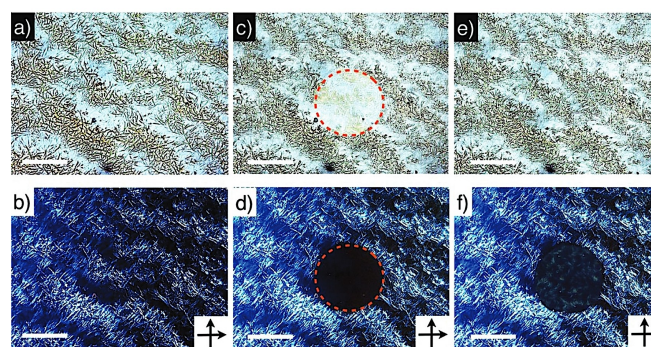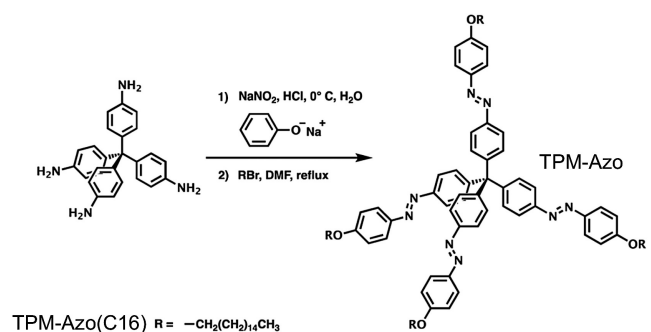

Figure 4. Top: synthetic scheme and structure of **TPM-Azo** derivatives. Bottom: polarizing optical photomicrographs of a sample of solid **TPM-Azo(C16)** under bright field (top) and cross-polarized (bottom) light illumination. Before (a and b) and after (c and d) near-UV irradiation (Hg lamp, Nikon UV-2A filter, bandpass: 330–380 nm) in a central spot (dashed red line) for 10 minutes (e and f). Recrystallization of the irradiated sample is observed upon thermal annealing at 130 °C for 20 min. Scale bar, 100 μm. The arrows in b), d) and f) represent the relative orientation of the polarizer and analyser. Reproduced with permission (Ref. [37]). Copyright 2019, Royal Society of Chemistry.

the size of the alkyloxy chain attached to the compounds taken into account, indicating that in the solid state the molecular arrangement is such that the alkyloxy chains are mobile and do not affect the photoreactivity.

2.3. Pyridylpyridinium and viologen derivatives

Pyridinium and bipyridinium chromophores were extensively studied for decades due to their photophysical and electrochemical properties,[38] since they can be used as electron acceptor recognition sites and redox active units in supramolecular systems.[39–41]

TPM was functionalized with pyridylpyridinium units (**TPM-PP**, Figure 5)[42] obtaining a tetrahedral shape-persistent multichromophoric system. Each of the pyridylpyridinium units is linked through the central carbon atom. DFT calculation disclosed that homoconjugation through the central carbon atom between each unit can occur, with orbital overlap of the π-system, as observed in other tetramers.[43] The result of this conjugation leads to a red shift of absorption (2350 cm^{-1}) and an enhanced fluorescence ($\Phi_{em}=40\%$) of the tetramer compared to the model monomer ($\Phi_{em}=0.4\%$). The rigidity of the structure of the tetramer and the conjugation through the central sp^3 carbon atom change significantly the properties compared to the monomer, increasing the radiative deactivation rate of the excited state of the tetramer.

A tetramer composed of four bipyridinium units (**TPM-MV**)[44] showing a tetrahedral shape-persistent structure was synthesised. This compound displays peculiar photophysical and redox properties in its ground and reduced states compared to its corresponding model compound (1,1′-dimethyl-4,4′-bipyridinium, **MV**).

As confirmed by computational studies, the absorption spectrum of the tetramer is not merely the summation of four bipyridinium units: the lowest energy electronic transition is observed at higher wavelengths compared to that of model compound and allows the population of a luminescent excited state. The emission of **TPM-MV** can be likely attributed to the fact that its rigid structure favors radiative deactivation of its excited state, in comparison to that of non-emissive **MV**.
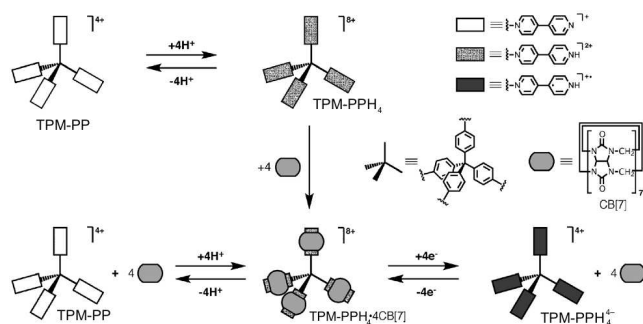
Each of the four viologen units of **TPM-MV** could be reversibly mono- and di-reduced at higher potentials than model compound **MV**. The monoreduced form of **TPM-MV** undergoes pimerization similar to **MV**.[45] Thanks to the rigid tetrahedral structure of the TPM scaffold each viologen units cannot interact with the neighbors, leading to the formation of a supramolecular structure (see Figure 6). Pimerization is favored by the TPM structure due to a cooperative mechanism: the tetramer with four monoreduced units is greatly stabilized by the multiple interactions in the supramolecular structure.

Furthermore, the free nitrogen atom of **TPM-PP** could be used as ligand to complex ruthenium porphyrins (Ru(CO)FTPP) by self-assembly of a giant multichromophoric architecture.[46] The assembly can be obtained in mild conditions at room temperature under stirring, as confirmed by X-ray diffraction analysis. After complexation the absorption spectra of the Ru(CO)FTPP subunit changes, observing a red shifted Soret band and a hypochromism of the Q-bands.

TPM-PP is itself highly emissive, but after coordination with Ru(CO)FTPP the emission intensity decreases indicating a quenching process. By electrochemical methods, the energy of the charge-separated state (CS) was estimated at about 1.80 eV, slightly lower than the triplet state (T$_1$) of the Ru(CO)FTPP moiety (E$_{00}=1.84$ eV). The Jablonsky diagram reported in Figure 7 shows the process occurring after excitation of the **TPM-PP** core. The S$_1$ excited state of the tetramer can be quenched by electron transfer (el. T) populating the CS state or by an energy transfer (en.T) to the S$_1$ of the Ru(CO)FTPP. The S$_1$ state of the latter can undergo an efficient intersystem crossing (ISC) and be converted into the triplet state T$_1$. The triplet excited state T$_1$ of the porphyrin is quenched by electron transfer only at room temperature, while at 77 K the energy of the CS state increases above the energy of the T$_1$ excited state, making endoergonic any possible electron transfer.

This example demonstrates that multichromophoric systems as **TPM-Ru** can be relatively easily self-assembled from

Figure 5. Schematic structure and acid-base controlled encapsulation of **TPM-PP** by CB[7]. Reproduced with permission (Ref. [42]). Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA.
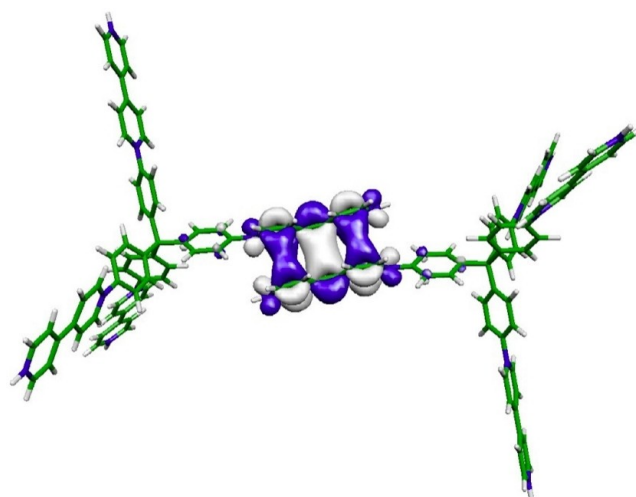
Figure 6. M06L/6-31G*-optimized geometry of the pimer of **TPM-MV** in water. The orbital responsible for pimer binding is also shown. Reproduced with permission (Ref. [44]). Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA.
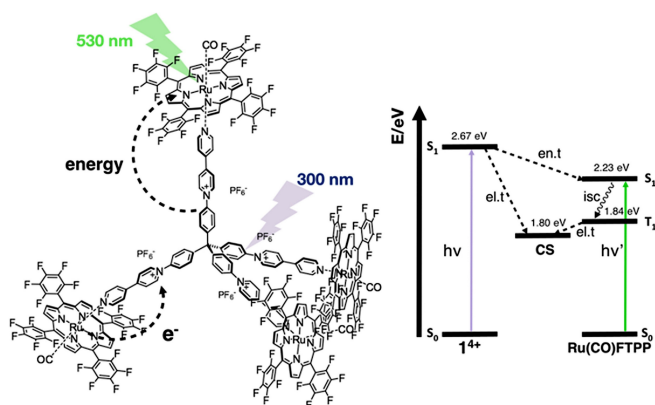
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Figure 7. A schematization of all the photophysical processes occurring in the supramolecular assembly of **TPM-Ru**. Reproduced with permission (Ref. [46]). Copyright 2021, Wiley-VCH Verlag GmbH & Co. KGaA.

pyridylpyridinum and porphyrin units. The photophysical properties could be further modulated varying the temperature or adjusted by different substituent groups on the porphyrin.

3. Tetraphenylethylene (TPE) derivatives

As mentioned in the previous sections, contrarily to the tetraphenylmethane scaffold, the tetraphenylethylene platform offers a rich and interesting combination of photophysical properties. As several other families of compounds, featuring peripheral aromatic units connected to a conjugated rigid core,[47] TPE belongs to the class of AIE-active molecules: in solution at room temperature the luminescence quantum yield of these chromophores is usually negligible, while a highly intense fluorescence is detected in experimental conditions in which molecular motions are prevented, favouring the radiative deactivation of the excited states in place of a thermal dissipation through vibrational or rotational motions.[48,49]

For this reason, TPE has been regarded in recent years as a useful molecular motif for the synthesis of a vast number of luminescent materials, for applications that include chemosensors (or generally in chemical structures whose photophysical properties respond to the increased rigidity of the system[50,51]), covalent- and metal-organic frameworks (COFs and MOFs),[52] cell imaging agents[53] and optoelectronic devices.[54,55]

Most importantly, the molecular scaffold provided by TPE offers a geometrically rigid arrangement that can be suitably connected covalently with multiple functional moieties (Figure 8). The latter include common luminophores, such as arenes,[56,57] rylenes,[58,59] carbazoles,[60,61] or metal complexes.[62] In recent times, this principle has been successfully applied in a series of supramolecular multichromophoric systems in which the photophysical properties of the peripheral units can be modulated by the TPE core upon the application of physical or chemical stimuli (e.g., absorption of light, ion coordination, application of an electric potential, etc).

In solution, the absorption spectrum of TPE shows high similarities to that of Z-stilbene, and it has been concluded that
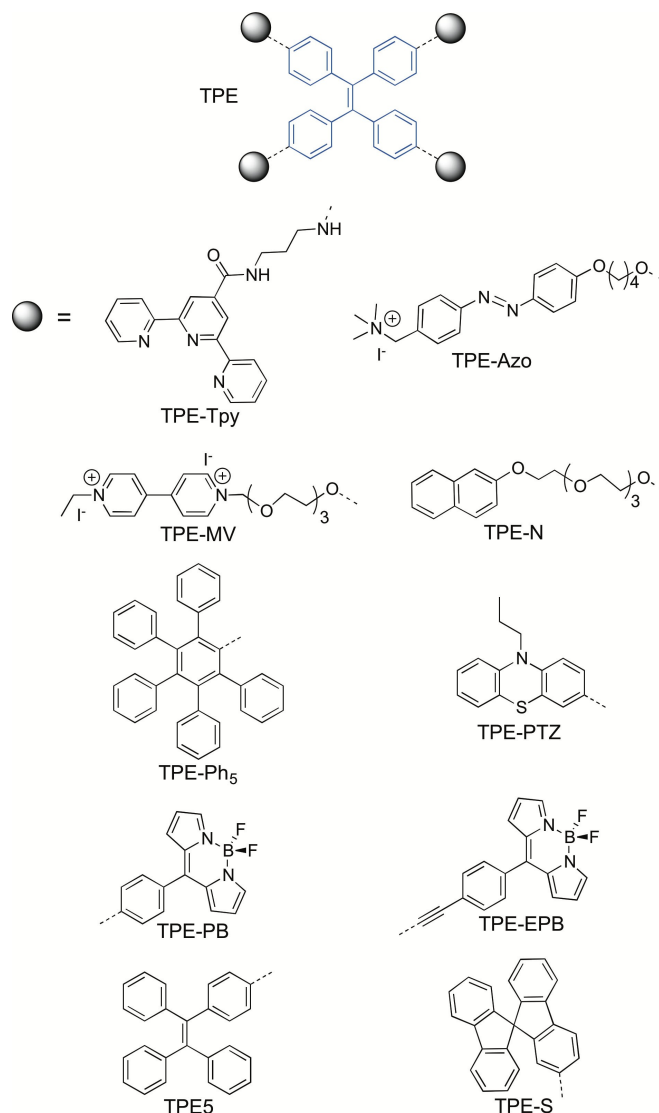

Figure 8. Schematic representation of the TPE derivatives discussed.

its most stable configuration is the one showing all the phenyl substituents tilted to some extent in comparison to the plane of the central ethylene core.[63] Upon its excitation, the photophysical deactivation of the lowest singlet state of TPE occurs by fluorescence, $E{\rightarrow}Z$ isomerization, intersystem crossing and eventual formation of dihydrodiphenylphenanthrene.

In solution at r.t. the fluorescence quantum yield (Φ_f) of TPE is in the order of 0.1%, while its lifetime is in the range of picoseconds.[63] Early reports on TPE derivatives presented how the decrease of torsional degrees of freedom of the rotating peripheral phenyl units play a crucial role in the radiative deactivation of the singlet excited state.[64,65] Samples containing TPE change dramatically their luminescence performance upon application of specific experimental conditions, as in rigid matrix[66] or in high viscosity media,[67] tracing the dependence between Φ_f and the probability and extent of the out-of-plane twisting motions of the phenyl subunits around the central double bond. As a consequence of the combinations of these

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factors, TPE is strongly emissive in the visible region (a light blue color is emitted, $\lambda_{max} \approx 475$ nm, $\Phi_f > 50\%$) in frozen rigid matrices, in the solid phase, or in colloidal suspensions formed in water at r.t., upon addition of the latter to a miscible solvent (typically CH_3CN, DMSO, or THF) in which the molecule is soluble.[68] Small but appreciable differences in the emission profiles are often detected as a consequence of the presence of amorphous and crystalline domains in the micro- or nano-sized colloidal particles.[69,70] Concerning their electrochemical properties, TPE derivatives show non-reversible double-electron reduction waves at low potentials (ca. -3.0 V vs. SCE)[71] and close first-to-second oxidation peaks ($\Delta E^{2+/+} < 0.2$ V).[72]

We introduce here a selection of examples in which the luminescence properties of multichromophoric TPE derivatives are modulated by the presence of different classes of substituent groups.

3.1. Tetrafunctionalized TPEs: polypyridyl (and related) ligands

Among the most common motifs in supramolecular chemistry, polypyridyl ligands can be grafted on the TPE core and induce some significant changes in its luminescent properties upon metal coordination. For a more detailed discussion on the metal coordination-induced AIE effects on TPE, the readers will be referred to a recent review by Yu, Han and coworkers, specifically covering this topic.[73]

The TPE core has been used in a coordination polymer gel with tunable emission (ligand **TPE-Tpy**),[74] in which the terpyridine ligands decorating the AIE-active core undergo metal coordination: in this example, the authors studied how the self-assembly processes arising from the combination of supramolecular interactions can induce changes in the luminescent properties. In the solid phase, the emission profile of **TPE-Tpy** is excitation dependent, indicating the presence of the two individual chromophoric units, emitting at $\lambda_{max} = 410$ and 480 nm, from the terpyridyl periphery and the TPE center, respectively. More specifically, when a H-bonding network results from the intermolecular interaction between the amide groups, the supramolecular assembly formed by **TPE-Tpy** shows an emission at $\lambda_{max} = 480$ nm, corresponding to the TPE emission; on the other hand, the stoichiometrically defined coordination of Eu(III) ions with **TPE-Tpy** (2:1 ratio, respectively) induces a hypsochromic shift of the emission spectrum, thus attributed to a combination of AIE and matrix coordination induced emissions. When coordinated by metal ions, the terpyridyl ligands are most likely able to decrease the planarization of the phenyl units of TPE, leading therefore to a smaller contribution of the latter to the emission of the assembly.

3.2. Azobenzene derivatives

In the search of new photoresponsive materials, the TPE scaffold was appended with four azobenzene units (**TPE-Azo**).[75]

By taking advantage of the host-guest interactions with pillar[6]arene in water, the fluorescence of the TPE core is restored upon addition of the macrocyclic receptor. This can be explained by the increased rigidity provided by the complexation of **TPE-Azo**; in addition, the authors claim that the same effect is due to the inhibition of photo-induced electron transfer (PET) efficiencies from the TPE unit to the threaded electron-poor azobenzene unit, despite the reduction potential of the latter should not be significantly affected by the presence of the macrocyclic complexing unit.[76] Furthermore, the emission of TPE core can be switched-off repeatedly upon irradiation of the [**TPE-Azo**·pillar[6]arene] complex in the visible region, causing the $E \rightarrow Z$ isomerization of the azobenzene units. The steric hindrance provided by the E isomer contributes to the release of the macrocyclic units, accompanied by the decrease of the emission intensity.

3.3. Methylviologen derivatives

The self-assembly of small building blocks based on the TPE motif can be achieved with introduction of supramolecular driving forces, ultimately able to drive a relevant physical property of the assembly – such as the luminescence – to change. Two four-armed TPE derivatives – containing naphthyl (**TPE-N**) and viologen groups (**TPE-MV**) – are able to associate in 1D nanorods (Figure 9) by exploiting charge-transfer (CT) interactions.[77] The so-formed supramolecular complex ([**TPE-N**·**TPE-MV**]) shows an enhancement of the emission intensity, due to the higher strain of the supramolecular assembly. The same principle was used in a ternary system including **TPE-N**, **TPE-MV** and the water soluble macrocyclic pillar[6]arene, joining together the AIE responsiveness of the two TPE derivatives and the pH sensitivity of the macrocycle. Specifically, the disassembly of [**TPE-MV**·pillar[6]arene] and the subsequent recovery of the AIE emission from [**TPE-N**·**TPE-MV**] have been demonstrated as useful diagnostic methods for the imaging of cancer cells.

3.4. Phenyl (or fully aromatic) derivatives

Extension of the aromatic branches with *p*-phenylene fragments does not dramatically affect the photophysical performances of
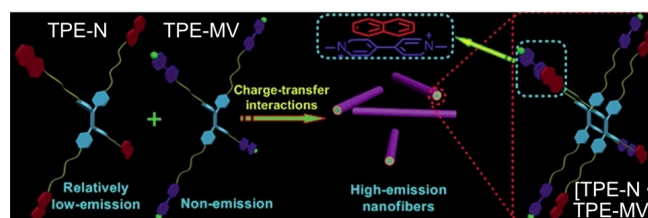

Figure 9. Schematic representation of the self-assembly process of **TPE-N** and **TPE-MV** to complex [**TPE-N**·**TPE-MV**] driven by charge-transfer interactions. Reproduced with permission (Ref. [69]). Copyright 2014, Wiley-VCH Verlag GmbH & Co. KGaA.

the fluorophore, with the energy of the lowest energy lying absorption and fluorescence (in the solid phase) bands weakly red-shifted and blue-shifted, respectively, compared to bare TPE. In addition, very weak emissions in solutions at room temperature are detected ($\Phi_f < 0.1\%$).[78] In tetrasubstituted TPE (**TPE5**), a slight increase of the quantum yield is observed in solution ($\Phi_f = 3.4\%$), most likely due to the increasing stiffness of the luminophore.[79] In another example, the dendritic scaffold **TPE-Ph$_5$**, obtained upon the full substitution of the plain TPE core with pentaphenyl functions, shows a relatively high intensity fluorescence ($\lambda_{max} = 520$ nm, $\Phi_f = 13\%$) in CH_2Cl_2 solutions at room temperature, while the monosubstitution product does not show any difference compared to pristine TPE, with a negligible emission quantum yield.[80] The emission profile of **TPE-Ph$_5$** is similar to that obtained from the parent tetrameric *p*-terphenyl derivative ($\Phi_f = 2\%$) and remains unchanged regardless of the excitation wavelength used. Furthermore, the similarity of the absorption spectra of **TPE-Ph$_5$** and that obtained by the sum of the five separated components suggests a weak electronic coupling between the peripheral and core chromophores. Overall, these results indicate that the presence of four pentaphenyl groups in **TPE-Ph$_5$** causes a sufficiently high strain to provide a restriction of molecular relaxation even in solution. Interestingly, the same considerations hold true taking into account further symmetrical extension of the aromatic system with an increasing number of *p*-phenylene units around the TPE platform.[81]

The photophysical properties of multichromophoric systems based on TPE depend on a combination of several factors and mainly determined by the nature of the excited state of the peripheral subunits. For instance, in the presence of electron-abundant phenothiazine, the absorption spectrum of tetra-substituted derivative **TPE-PTZ** shows a charge transfer (CT) character, which accounts for the significant solvatochromism of the molecule.[82] **TPE-PTZ** is luminescent in THF solutions at r.t. and shows a bathochromic shift of its AIE emission, corresponding to that arising from aggregates, in the presence of high amounts of water. Similar compounds have also been reported as optically active materials in solution-processable OLEDs.[83]

In a recent report, the tetrasubstitution of the TPE core with BODIPY (boron-dipyrromethene) subunits – distanced by aromatic spacers of different lengths – was reported as a strategy to yield efficient luminescent materials both in solution and in the solid phase.[84] A preliminary photophysical analysis showed that, upon excitation of the BODIPY moiety, the emission spectrum of compound **TPE-PB** is similar to that recorded from the isolated BODIPYs when it is dissolved in solution or when microaggregates are obtained by the addition of a non-solvent (i.e. H_2O). The resulting emission profile seems not affected by the presence of the attached TPE scaffold; however, analysis of the excited state's lifetime and luminescence quantum yield would be necessary to assess a clearer description of possible intramolecular quenching mechanisms (namely energy and electron transfer). On the other hand, in the presence of high concentrations of H_2O, compound **TPE-EPB** shows a considerable decrease of the BODIPY emission and
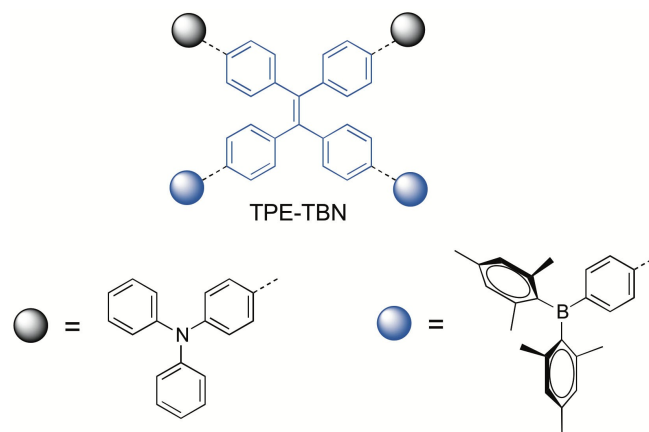

Figure 10. Schematic representation of the unsymmetric TPE derivatives.

a concomitant increase of the emission intensity at $\lambda_{em} = 645$ and 730 nm, while the typical emission profile of TPE is not detected. This could be indicative of the presence of several π-π stacking modes in the aggregated state of **TPE-EPB**, as evidenced for other diarylethene derivatives.[85] Along these lines, the functionalisation of TPE's peripheries with conventional luminophores generally leads, in comparison to the corresponding free entities, to weak emission intensities in solution ($\Phi_f < 5\%$),[59] pointing out the occurrence of effective quenching mechanisms. This is observed for instance in the presence of four spiro-bifluorenyl groups (**TPE-S**, $\Phi_f = 2.9\%$ in dioxane),[79] while once more the emission quantum yield in the solid state results markedly increased.

Asymmetric heterosubstituted star-shaped TPE derivatives containing triphenylamino and triarylborane groups (**TPE-TBN**, figure 10) have also been reported for their AIE behaviour and their application in non-doped OLEDs.[86] Similarly to the previous examples with homogeneous substitutions, these asymmetric counterparts can show a remarkable enhancement of the emission quantum yield by moving from solutions to solid state films. Density-functional theory (DFT) calculations pointed out the scarce conjugation between the substituents, with HOMO and LUMO densities distributed on the electron-rich triphenylamino and the triarylborane acceptor, respectively.

4. Conclusion and perspectives

TPM is a rigid scaffold with tetrahedral shape, characterised by absorption and fluorescence bands in the UV spectral region and high-energy reduction and oxidation processes: these properties make it an innocent scaffold for supramolecular chemistry and multichromophoric systems. Four chromophoric units could be appended to the phenyl ring, like in the examples reported. In perspective, due to the easy chemical functionalization on its extremities and precise spatial allocation of the peripheral units, molecular materials based on the TPM scaffold could show suitability in a vast range of technological applications, such as chemo- and physically responsive porous

materials (e.g., COFs and MOFs), photoswitchable supramolecular receptors, inclusion complexes or cages. The rigidity of the structure enhances the luminescence (**TPM-PP**) or enables the formation of supramolecular structures by external stimuli (**TPM-Tpy**, **TPM-MV**). The central sp^3 carbon allows conjugation between the four arms of the structure, affecting and changing the photophysical properties of the tetramer compared to the monomer (**TPM-MV**, **TPM-PP**). In comparison, for the corresponding TPE congeners, experimental results based on absorption and emission spectroscopies rarely detect significant electronic coupling between periphery and core.

In most examples reported featuring TPE derivatives, the luminescence properties stem essentially from the inherent behaviour of their AIE-active core, which allows to obtain a modulation of the spectral response in different physico-chemical conditions. Yet, the electronic interactions both at the ground and excited states between peripheral and core units, which might be responsible of an excitation-dependent emission, are often overlooked. This ultimately does not allow a precise identification of advantages vs. drawbacks in using peripheral chromophores of a specific nature, since TPE derivatives containing them virtually display the same photo-physical behaviour. The same conclusions can be drawn by taking into account the frequently disregarded electrochemical properties, since they can be crucial in the evaluation of the electronic interactions occurring between the components of the supramolecular system under examination. On the other hand, it is also worth highlighting that the design of AIE-active functional materials has to take into account an intricated merger of different contributions which can preferentially lead to mechanisms of luminescence quenching or enhancement, especially in the solid phase where specific intermolecular interactions can occur.[87,88] Concerning the energy of the emitting excited state of TPE derivatives, a combination of factors – i) degree of conjugation between TPE core and periphery ii) CT character of the excited state iii) planarisation in the excited state, among others – results in batho- or ipsochromic shifts of the fluorescence of the solid phase compared to the molecule in solution.[89,90] A comprehensive depiction of the photophysical processes involved in the luminescence of this class of multichromophoric materials will help to find relevant applications that could take advantage of their peculiar aggregate-dependent luminescence, such as in sensors for the transduction of mechanical forces into a light signal, in bioimaging devices or tunable optoelectronics.

While a huge amount of literature has been recently produced, containing some enticing and inspiring examples, there is still room for improvement for a clear understanding of the underlying photophysical phenomena involved in such supramolecular systems. To conclude, both TPM and TPE scaffolds could be considered for applications when a rigid structure with a low degree of conjugation between the chromophoric units is needed. This peculiarity enhances the photophysical properties of the chromophoric units and provides the possibility of forming supramolecular assemblies. The TPE scaffold will be preferred for applications where the presence of chromophoric units could modulate the AIE proper-ties of the core, as a consequence of the formation of supramolecular assemblies or of a solid phase.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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