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# Triarylamine-based Supramolecular Polymers: Structures, Dynamics, Functions

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## CONSPECTUS

Triarylamine molecules and triarylamine-based covalent polymers have been extensively investigated for more than sixty years in academics and industry because of their intriguing electronic and optical characteristics. However, despite the profusion of studies made on these derivatives, only very recently have the first examples of supramolecular polymers based on the triarylamine motif been described in the literature. Specifically, our research group has shown that, by adding supplementary hydrogen bonding moieties such as amide functions in their periphery, it becomes possible to tightly pack triarylamine molecules in columnar supramolecular stacks presenting a collinear arrangement of their central nitrogen atoms. These supramolecular polymers can self-assemble into various soft hierarchical structures such as helical fibers, nanorods, nanospheres, and nanoribbons in the sol and in the gel states, into liquid-crystalline mesophases, as well as into highly organized supramolecular frameworks and their single crystals thereof. Interestingly, the associated supramolecular polymerization mechanism involves a nucleation step

of high activation energy which requires the flattening of the triarylamine core. Because of this singularity, and although dependent on the precise chemical nature of the building blocks, it has been demonstrated that their supramolecular polymerization can be triggered by original tools such as light irradiation or electrochemistry, and that it can display autocatalytic growth behaviors, remarkably strong amplifications of chirality, as well as complex and competing thermodynamic and kinetic self-assembly pathways. Further, from a functional point of view, it has been highlighted that a partial oxidation of the triarylamine molecules results in an enhanced through-space delocalization of the charge carriers along the  $\pi$ - $\pi$  stacked supramolecular polymers, a feature that confers to these nanowires exceptional transport properties. Upon increasing the charge carrier concentration, the electronic nature of these soft materials can be switched from a semiconducting to a metallic behavior, and the presence of highly delocalized unpaired electrons in supramolecular polaronic band structures has been further exploited to implement plasmonic properties within subwavelength organic interconnects and microscopic optical waveguides. Finally, by making use of the unusual dynamics and functions of triarylamine-based nanostructures, it becomes possible to precisely address their self-construction within confined environments or within nano- and micrometer scale devices. This has been demonstrated for instance in between nanoparticles and in between electrodes, inside inorganic nanopores and inside phospholipid bilayers, as well as at the liquid-liquid interface. Such a meeting point between bottom-up and top-down technologies is of high interest to envision further developments and applications for this entirely new class of supramolecular polymers which combine a unique relationship between their structures, their dynamics, and their subsequent emerging functional properties.

## MAIN TEXT

### 1. Introduction

Triarylamine (TAA) derivatives represent a well-known class of organic molecules constructed around the triphenylamine (TPA) core. They have been intensively used for decades because of their properties as electroactive and photoactive materials.<sup>1,2</sup> In 2010, our research group discovered that some TAA derivatives – *i.e.* TAA substituted with at least one lateral amide group – can undergo supramolecular polymerization.<sup>3</sup> In this original report, we provided the first structural description of TAA-based supramolecular polymers which was later on revealed as a general feature for a large family of analogues. The main characteristic of these supramolecular polymers is a columnar packing of TAA units with a collinear arrangement of their central nitrogen atoms. This supramolecular structure is mostly stabilized by a combination of *i*)  $\pi$ - $\pi$  stacking interactions between the phenyl groups of the TAA, and of *ii*) hydrogen bonds provided by their lateral amide groups. In the present account, we will first describe in detail the various columnar TAA structures that have been published in the literature so far. In particular, we will highlight how the precise molecular nature of the TAA can influence fine local variations of their primary packing, as well as their various hierarchical organizations at higher length scales. We will then describe the supramolecular polymerization mechanisms that have been proposed depending on the TAA molecular structures and on the environmental conditions imposed to the systems. We will finally show that TAA supramolecular polymers provide an original platform for a number of intriguing functional features including ionic, electronic, and photonic transport properties.

## 2. Structural aspects of triarylamine-based supramolecular polymers

The primary structure of TAA-based supramolecular polymers is governed by a limited number of parameters, but their combination can lead to important variations which influence the polymer chirality, its self-assembly mechanism, its mesoscale organization, as well as its functional properties. It is thus of crucial importance to understand the basic relationships that link the molecular configuration and conformation of TAA molecules with their supramolecular structures. Three main molecular parameters have been shown to modify the primary packing of TAA units: *i*) their chiral conformation, *ii*) the number of amides substituting the TPA core, and *iii*) the nature of the solubilizing chains at their periphery.

The chiral conformations of TAA molecules are enforced by the fact that the phenyl rings of the TPA core have to rotate out of the molecular main plane in order to get rid of steric repulsions between them. As a result, TAA molecules are chiral propellers with two limit conformational enantiomers  $\lambda$  and  $\lambda$  (Figure 1A). As suggested early by our experimental observations and theoretical approaches together with Semenov,<sup>3,4</sup> the mutual attraction between aromatic rings of TPA propellers can result in two distinct conformations of very similar energies and which share a comparable collinear arrangement of their central nitrogen atoms. In the “snowflake” situation, TPA cores alternate their  $\lambda$  and  $\lambda$  chirality – thus leading to a global achiral supramolecular columnar packing – and display a rotation angle of 60° together with a N-N distance of 0.48 nm between two stacks (Figure 1B*(i)*). Such a snowflake conformation was for the first time observed experimentally in 2010 on double columns of TAA *mono*-amides.<sup>3</sup> In the “Mercedes-Benz” situation, TPA cores of similar chirality are stacked with a N-N distance of 0.5 nm between them and with a minimal rotation angle of 1.5°, leading to either *M* or *P* helicities for a given supramolecular column (Figure 1B*(ii)*). Such a helical conformation was for the first time observed

experimentally in 2014 on single columns of triarylamine *tris*-amides (TATA).<sup>5</sup> Importantly, in both the achiral and chiral supramolecular columns, because of the out-of-plane tilt of the propeller phenyl rings, and despite an average distance between the nitrogen centers of  $\sim 0.48$ – $0.50$  nm, additional short distances of  $\sim 0.31$ – $0.36$  nm were measured by small angle X-ray scattering (SAXS). They correspond to edge-to-face  $\pi$ - $\pi$  stacking of the TPA cores in the snowflake conformation, and to face-to-face  $\pi$ - $\pi$  stacking of the TPA cores in the Mercedes-Benz one.<sup>4,5</sup>

The number of amide substituents on the TPA core is also an important parameter to understand the stacking behavior as well as the thermodynamic and kinetic stabilities of their corresponding supramolecular polymers. The amide functions can either interact with one another along a single supramolecular column, or between distinct columns by lateral interactions. For instance,  $C_3$ -symmetric TATAs with bulky lateral alkyl chains have been shown to usually produce single columnar arrangements made of Mercedes-Benz stacks connected by three infinite strings of intra-columnar hydrogen bonds. To adapt the characteristic hydrogen bond distance with the N-N distance, the rotational angle between two consecutive stacks was experimentally shown to increase up to  $20^\circ$  (as compared with the  $1.5^\circ$  of a simple TPA model), therefore decreasing the pitch of the corresponding helical polymer (Figure 1C).<sup>5-8</sup> It should be noted that carbonyl-bridged triarylamine *tris*-amides, presenting an achiral flat TPA core substituted with large chiral alkyl chains, also lead to similar helical supramolecular polymers.<sup>9,10</sup> In striking contrast, the use of similar  $C_3$ -symmetric TATAs with a minimal steric hindrance – *i.e.* with three amides substituted by methyl groups – leads to a snowflake conformation and to a highly ordered 3D supramolecular framework organized by inter-columnar hydrogen bonds, as recently characterized by X-ray diffraction (XRD) of single crystals (Figure 1D).<sup>11</sup> In the case of *mono*-amide TAA derivatives, only snowflake conformations were characterized by SAXS and XRD to date, revealing that the

amide groups are here instrumental to self-assemble two columnar stacks along a zipper-like string of hydrogen bonds (Figures 1E).<sup>4,12</sup>

Going further, the primary structures of these monodimensional supramolecular polymers can often lead to higher order aggregation processes which produce gels, mesophases, and colloidal mesostructures of various aspects. The mesoscale organization was shown to be dependent on several factors including the steric bulkiness of the TAA monomers, the mutual affinity of their substituents ruling lateral aggregations, the contour and persistence length of the primary fibrils, the number of TAA moieties contained in the monomer, *etc.* Obviously concentration and temperature also play an important role as it is the case for any supramolecular self-assembly. Interestingly, TAA derivatives were shown to produce columnar stacks even when bearing very large substituents in solution,<sup>13-16</sup> in thin films,<sup>14,17</sup> or in the bulk with the formation of various liquid-crystalline mesophases (Figure 1F).<sup>18,19</sup> Strikingly, even when TAA are conjugated to substituents as large as fullerene moieties, 1D or 3D supramolecular polymers can be obtained (Figure 1G).<sup>20,21</sup>

Overall, after a few years of investigations, more and more evidence highlights that the propensity of TAA derivatives to stack with one another embodies a quite general rule. As soon as the TPA core is substituted with at least one amide group, it appears very tolerant to a number of supplementary chemical modifications and it tends to form supramolecular polymers. To go further with the basic knowledge and potential implementations of these self-assemblies, it appears of first importance to better understand the thermodynamic and kinetic parameters that govern their supramolecular polymerization.

### 3. Dynamic aspects of triarylamine-based supramolecular polymers

#### 3.1 Supramolecular polymerization of triarylamine mono-amides

The first mechanistic investigations on the supramolecular polymerization of triarylamines were performed with TAA *mono*-amides.<sup>4</sup> This was motivated by the intriguing behavior of molecule **1** in chloroform ( $c \approx 1 - 10$  mM) (Figure 2A). Although highly stable when kept in the dark, the yellow solution turns slightly green when exposed to visible light for a few minutes. This color change is caused by the production of a small quantity (typically between 0.1% and 1%) of triaryl-ammonium radicals **1**<sup>+</sup> (Figure 2A), which subsequently triggers a supramolecular polymerization process leading to the nanorods shown in Figure 1E(iii).

This polymerization was shown fully reversible by using thermal heating or dissociating solvents. The involved mechanism was studied in depth by a large combination of experimental and theoretical tools, and it was shown to proceed as follows (Figure 2B). The first activation step is related to the metastable character of unimer **1** because of its conformation. Indeed, neutral **1** adopts a slightly pyramidal conformation of its  $sp^3$  nitrogen center with a strong out-of-plane rotation of the aromatic rings which avoid polymerization on its own. However, **1**<sup>+</sup> becomes flat on its  $sp^2$  nitrogen center and the ring rotation angles decrease significantly (Figure 2B(i)). We further detailed how the flat radicals form strings of dipoles with  $Cl^-$  and then facilitate dipole-dipole and stacking interactions, and how TAA combine in a snowflake conformation to produce hydrogen-bonded double columnar nuclei involving six molecules of **1**<sup>+</sup> from an extremely low critical concentration of  $10^{-8}$  M (Figure 2B(ii)). Once double columnar nuclei are formed, they can attract neutral TAA **1** because the energy gain of attachment is now sufficient to flatten the free propellers from the solution (Figure 2B(iii)). Therefore, the nucleation step provides a platform



for the end-growth of the double-columnar supramolecular polymer that can in turn bundle in larger fibers and nanorods by making use of van der Waals interactions provided by lateral alkyl chains (Figure 2B(iv)). Interestingly, the same supramolecular polymerization process can be triggered in the absence of light but in the presence of a catalytic quantity of chemical oxidant (tetrabromoquinone), or by seeding the solution of TAA unimers with a catalytic quantity of preformed fibers in suspension. In these three modes of activation (light, chemical oxidant, and seeding) it was shown that sigmoidal aggregation profiles are obtained with lag times that can reach more than one hour for very low quantities of activator (Figure 2C(i)). This autocatalytic – self-replicating – behavior was modeled by a universal equation taking into account the nucleation rate and the scission rate of the fibers which contribute to the acceleration of the process by increasing over time the concentration of polymer ends on which free neutral unimers can associate. This general model of nucleation/growth was further confirmed using advanced light scattering experiments (Figure 2C(ii)),<sup>22</sup> and several other light-triggered supramolecular aggregations of *mono*-, *bis*-, and *tris*-amide TAA derivatives were additionally reported independently in the literature.<sup>14,23,24</sup>

Interestingly, the analytical equations supporting our model also indicate that the length of the polymer chains decreases for higher oxidation levels (and thus for higher light intensity), whereas the number of nuclei (and therefore the number of fibrils) increases.<sup>4</sup> This was for instance illustrated by irradiating TAA-fullerene conjugates with different light sources.<sup>20</sup> It was shown that with a halogen lamp, the quantity of generated radicals (and the number of nuclei) was small, thus leading to long supramolecular columns coagulating in larger ribbons (Figure 2D(i)). However, when using UV light at the same concentration, the high number of nuclei leads to short rods of about 10 stacks, which in turn hierarchically aggregate in micrometric spheres (Figure

2D(ii)). This example illustrates the interest to deeply understand such nucleation/growth mechanisms in order to tune the morphologies of supramolecular polymers at various length scales.

Further, we recently proposed that the initial light-irradiation step can also be replaced by a direct electrochemical oxidation, and we reported what can be considered as the first example of a “supramolecular electropolymerization” process.<sup>25</sup> The mechanism involved is very similar to the one proposed in Figure 2B, but with the nuclei being here produced by electro-oxidation at the anode. Interestingly, solvents with a low dielectric constant were used to trigger the nucleation at the anode surface only and, subsequently to directly interconnect the anode with the cathode by precisely orienting the fibers growth in the electric field, as demonstrated in microelectronic devices of various configurations such as ITO cells or interdigitated electrodes (Figure 2E(i-iii)). This unprecedented spatial precision of the supramolecular polymerization was demonstrated by bridging microarray electrodes of less than 5  $\mu\text{m}$  in diameter and over a distance of 50  $\mu\text{m}$  in length (Figure 2E(iv)).

### 3.2 Supramolecular polymerization of triarylamine tris-amides (TATA)

TATA molecules tend to stack more easily than their monoamide counterparts as they are less metastable in ambient conditions. We demonstrated for the first time in 2014 that solutions of TATA can stack in a racemic mixture of well-defined *M* and *P* helical supramolecular polymers, even at low concentration and room temperature, and that such supramolecular polymers can produce thermoreversible physical gels at higher concentrations (Figure 3A).<sup>5</sup> The remarkable stability of these structures, and their propensity to polymerize without external trigger, are permitted by the supplementary set of hydrogen bonds compared to their *mono*-amide

counterparts. Although being crossed spontaneously, the activation barrier related to the flattening of the propeller core in TATA is still present, and is partly responsible for large thermal hysteresis in the polymerization processes. While organogels based on TATA were previously reported in one paper of the literature, no suggestion of a supramolecular structure was made at that time.<sup>26</sup>

Recently, based on the demonstrated helical nature of the TATA stacks,<sup>5</sup> a number of mechanistic studies related to their supramolecular polymerization were published by several research groups.<sup>6,8,23,27–31</sup> For instance, by adding chiral side chains to the TATA core, Miyajima and Aida demonstrated the possibility to control the *M* or *P* helicity of the corresponding supramolecular polymers, and further to fully bias the handedness of a racemate of supramolecular helices made of TATA having no chiral side chains by using only 0.2 mol% of enantiopure TATA (Figure 3B).<sup>6</sup> The control of 500 soldiers by only 1 sergeant represents an unusually strong amplification of chirality attributed to the peculiar dynamics of the TATA propellers. The sensitivity of chiral TATA derivatives to environmental parameters was also nicely demonstrated by Jung and collaborators, who have revealed correlations between solvent properties and the selective expression of either left-handed or right-handed helicities in organogels.<sup>27</sup> Interestingly, Kim and collaborators published a study in which they observed a full control on the supramolecular chirality of TATA helices by simply using visible circularly polarized light (CPL).<sup>23</sup> Indeed, irradiation of TATA in chlorinated solvents with *r*- or *l*-CPL induces their self-assembly with opposite chirality, and moreover the resulting handedness could be totally switched by irradiating with a CPL of the opposite rotational direction (Figure 3C).

In parallel, the group of Meijer highlighted a number of very interesting mechanistic aspects. For instance, they proved that the helicity of single supramolecular columns in solution can be switched to the opposite handedness as a function of temperature (Figure 3D).<sup>8</sup> The related

cooperative nucleation/growth process was shown to produce a given helicity at high temperature, whereas the opposite helicity was obtained when cooling down the system below room temperature through a transition from the first assembled state. The helical transformation was attributed to a molecular conformational inversion of the TATA coupled to an internal helical inversion of the entire column, *i.e.* taking place without a depolymerization step as suggested by the unusually sharp transition observed when cooling the system. Meijer and collaborators also demonstrated that, in the case of monocolumnar systems made of flat carbonyl bridged TATAs, isodesmic and nucleation/growth pathways can coexist, and that each enantioselective pathway can be selectively accessed by processing the temperature profile.<sup>10</sup> In addition, our group demonstrated that the cooling rate used to induce the gelation of some TATA derivatives can modify the hierarchical chirality expressed at the supramolecular level (Figure 3E).<sup>30</sup> Indeed, we observed that, whereas *P*-helical fibers were formed from a toluene solution by fast cooling, *M*-superhelical fibers were produced upon slow cooling. Temperature-dependent CD measurements revealed a large thermal hysteresis (due to the activation energy necessary to flatten the chiral propellers), as well as strong memory effects illustrating an unusually complex stepwise combination of primary and secondary nucleation events that are at the origin of this structural bifurcation. These last results illustrate that pathway complexity in supramolecular polymerization can be encountered in systems which produce similar primary nucleation steps and primary growths, but which diverge when reaching their secondary or higher organizational order. Finally, Meijer and Palmans recently made use of the dynamics of TATA derivatives to construct supramolecular block copolymers under thermodynamic equilibrium conditions.<sup>28,29</sup> By using original super-resolution microscopic techniques, they revealed that block copolymers can be formed either by mixing preassembled homopolymers, or by copolymerization of monomers under

slow cooling (Figure 3F). The stability of the multiblock structure was shown to be governed by the fine balance between favorable hydrogen-bonding interactions and small mismatch penalties between two different monomers that avoid complete mixing.

To summarize, a number of recent studies have been performed to understand the mechanisms at work in the supramolecular polymerization of TAA derivatives. The propeller shape of the TAA core plays here again a central role as it requires the crossing of a high energy barrier to allow stacking, and as it drives the chirality of the self-assembly. It also provides a number of possibilities to play with thermodynamically stable and metastable states in order to access different polymer morphologies, or in order to trigger the polymerization by various external effectors such as temperature, concentration, light, chemical oxidants, seeding, or even electric field. These tools afford new possibilities to gain spatial and temporal precision in the supramolecular polymerization processes and, as illustrated in the next section, they also offer new opportunities to provide TAA-based materials with advanced functionalities.

#### **4. Functional aspects of triarylamine-based supramolecular polymers**

Our group early suggested that the red-ox properties of TAA derivatives, if combined with their ability to stack along continuous supramolecular pathways of overlapping  $\pi$ -orbitals, should potentially lead to hole-transporting materials.<sup>3</sup> The initial experimental evidence of such properties was published in 2012 by performing the direct self-assembly of TAA in between gold nanoelectrodes separated by a distance of 80 nm.<sup>32</sup> The fabrication process took advantage of the *in situ* supramolecular polymerization triggered by light of a chloroform solution in the presence of an electric field (Figure 4A(i)). The first interesting aspect is that charged TAA nuclei are attracted to the electrode, and that subsequent supramolecular growth follows the electric field

lines until bridging the entire gap. This self-construction process produces a highly ordered array of nanowires as probed by AFM (Figure 4A(ii)). The second interesting aspect is the outstanding conducting properties measured for such organic interconnects, with a striking increase of the conductance by six orders of magnitude during the supramolecular closure of the gap (Figure 4B(i)). In addition, the nanowires display ohmic conductivity of  $5 \times 10^3 \text{ S.m}^{-1}$  and sustain a current density of  $2 \times 10^6 \text{ A.cm}^{-2}$ , which are exceptional performances taking into account the interface contact (Figure 4B(ii)). It was also highlighted, by lowering the temperature down to 1.5 K, that the sum of ohmic contact resistance and intrinsic resistance of the organic supramolecular polymer display a metallic character (*i.e.* with a large density of freely moving charges within the nanowire). Such characteristics are exceptional for purely organic nanostructures and are only surpassed by ballistic carbon nanotubes with highly transparent resistance contacts. Based on these results, theoretical approaches on identical TAA stacks were performed independently by the group of Sanvito using density functional theory (DFT).<sup>33</sup> Their study confirmed that TAA nanowires are remarkable hole conductors, with a theoretical upper mobility as high as  $12 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ , a rather large value for any one-dimensional object (except for carbon nanotubes). Experimentally, very high conductivities were also reported for TATA in the gel state.<sup>5</sup> We showed that such materials can be switched from a semiconducting to a conducting behavior when doped by light irradiation. Various signatures of enhanced charge transport were evidenced upon photodoping, revealing for instance a half-filled polaronic band structure of the nanowires, the presence of temperature-independent delocalized Pauli spins, and a metallic reflectance (Figure 4C). The observation of such supramolecular (*i.e.* through space) polarons is of high novelty and interest, especially within a soft healable organic material. Interestingly, the groups of Kumar and Stupp reported independently the improvement of solar cells by implementing TAA

supramolecular polymers within the active layer.<sup>14,17</sup> In thin films, supramolecular columnar liquid crystals made of TATA can act as a switchable charge injection barrier by combining semiconducting and dipolar functionalities.<sup>19</sup> Besides, TAA nanowires were built within insulating mesoporous silica layers in order to access an hybrid conducting material functioning as a biocathode.<sup>34</sup>

In a complementary direction, the group of Sanvito investigated by DFT and Monte Carlo simulations the ability of TAA nanowires to behave as organic semiconductors for spintronic applications.<sup>35</sup> They reported on the finding of a spin diffusion length of 100 nm at room temperature, a rather large value compared to other organic materials. Independently, Meijer and Naaman first implemented TATA derivatives to control electrons' spin in a water splitting photoelectrochemical cell in order to suppress the undesired production of H<sub>2</sub>O<sub>2</sub> coming from the recombination of OH<sup>•</sup> radical.<sup>36</sup> For that, they coated anodes with chiral TAA supramolecular polymers in order to control the spin state of the electronic potential on which the reaction occurs. In this configuration, the spins of the hydroxyl radicals are aligned in a parallel fashion by the helical structures, so that their recombination into H<sub>2</sub>O<sub>2</sub> cannot take place and thus water splitting is enhanced (Figure 4D).

Optical properties of TAA-based supramolecular polymers have also emerged recently as an intriguing domain of investigations. For instance, a straightforward consequence of the stacked configuration is the appearance of an aggregation induced emission behavior in the visible region upon polymerization ( $\lambda_{\text{max}} \approx 500$  nm),<sup>10</sup> related to the locking of the free rotations in the propeller. This was implemented with the light-triggered self-assembly of TAA-based nanospheres for sensing explosives with detection limits as low as 120 nM.<sup>28</sup> A more unusual optical property of TATA columns is their capacity to transport light energy over extremely long distances. For

instance, Hildner and Schmidt proved possible to transport excitons over 4  $\mu\text{m}$  at room temperature within a single columnar fiber made of carbonyl-bridged TATA H-type aggregates (Figure 4E).<sup>14</sup> The experimental observations suggest a coherent transport mechanism and make these supramolecular polymers promising candidates for light-harvesting and quantum information technologies. In addition, our research group observed waveguiding properties in single crystals of TATA over distances larger than 10  $\mu\text{m}$ .<sup>16</sup> Here, the mechanism proposed to explain such a long range transport was correlated with the presence of metallic electrons in the doped crystals as revealed by their optical, electric, and magnetic properties (Figure 4F,G). Because the waveguiding observed does not amount to a photoluminescence mechanism, we proposed the partial involvement of a plasmonic mechanism. Such an active mechanism couples the incident light and the delocalized metallic electrons within the structures, akin to what is commonly observed in metallic nanowires. This explanation is in agreement with the fact that the energy transport occurs *i*) only when the crystals are excited by the laser source at their tips, and *ii*) with different laser excitation wavelengths, even in regions where the crystal does not absorb. Plasmonic transport was also proposed to explain the optical behavior of hybrid nanostructures connecting arrays of gold nanoparticles by doped TATA nanowires (Figure 4H).<sup>37</sup> In such devices, the optical conductivity of the plasmonic layer increases by about 20 times when compared to the undoped layer, suggesting an efficient exchange of metallic electrons between the gold nanoparticles through the subwavelength organic interconnects. As a whole, the optical properties of TAA-based materials appear extremely exciting for a number of new fundamental endeavors and potential applications.

Finally, one should also mention that TAA derivatives can take advantage of their intrinsic dynamic organizational properties to drive the formation of complex self-assemblies within soft



confined spaces. For instance, we have shown that photo-doped fibers of TATA can orientate upon centrifugation in large nematic domains at the chloroform/water interface, and subsequently drive the perfect alignment of strings of oppositely charged gold nanoparticles on their top (Figure 4I).<sup>12</sup> In a totally different approach, we have also demonstrated in collaboration with Barboiu and Lehn that TAA substituted with crown ethers can be stacked in confined phospholipid bilayers to form artificial potassium channels (Figure 4J).<sup>17</sup> XRD on single crystals revealed that a wire made of alternating  $K^+$  cation and water molecules is formed during the transport process, as observed in biology for the KcsA potassium channel.

## 5. Conclusions

This account describes the discovery of a new family of supramolecular polymers based on the stacking of triarylamine units. It highlights that they can tolerate a large variety of molecular variations and that their formation can be understood by a set of common general rules. The rich thermodynamic and kinetic characteristics of the triarylamine monomers lead to a large collection of self-assembly pathways including nested hierarchical dynamic structures, and permit original modes of activation and control. Further, their emergent electronic, magnetic, and optical properties reveal unprecedented behaviors of great fundamental value and of high potential interest for their implementation as new functional materials. Thus, triarylamine-based supramolecular polymers appear not only as a new class of supramolecular objects, but they also stimulate our imagination by pushing further the boundaries of the current scientific knowledge.

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### **Notes**

The authors declare no competing financial interests.

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† This Accounts is dedicated to the memory of our friend and co-author Joe Armao, one of the most brilliant young scientists we have met, and who left us on November 20<sup>th</sup> 2018.

## **BIOGRAPHICAL INFORMATION**

Emilie Moulin completed her PhD under the supervision of Prof. Nicolas Winssinger and pursued her post-doc in the group of Prof. Alois Fürstner. Since 2008, she holds a Chargé de Recherche position at the CNRS and is an expert in synthetic and supramolecular chemistry.

Joseph J. Armao IV was born and educated in San Diego. He did his PhD under the supervision of Prof. Nicolas Giuseppone and pursued his scientific training by a post-doctoral stay with Prof. Jean-Marie Lehn. His interests range from science in general to philosophy.

Nicolas Giuseppone is distinguished Professor of chemistry at the University of Strasbourg and member of the Institut Universitaire de France. His research interests are focused on supramolecular chemistry, molecular machines, and functional materials.

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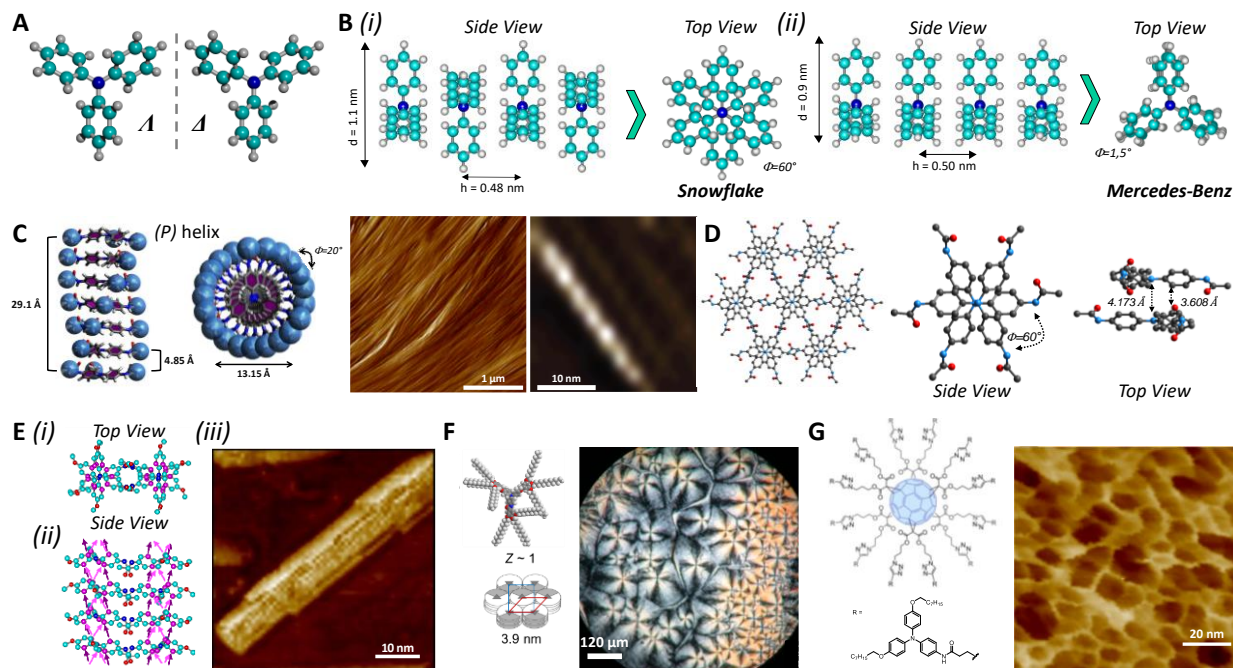
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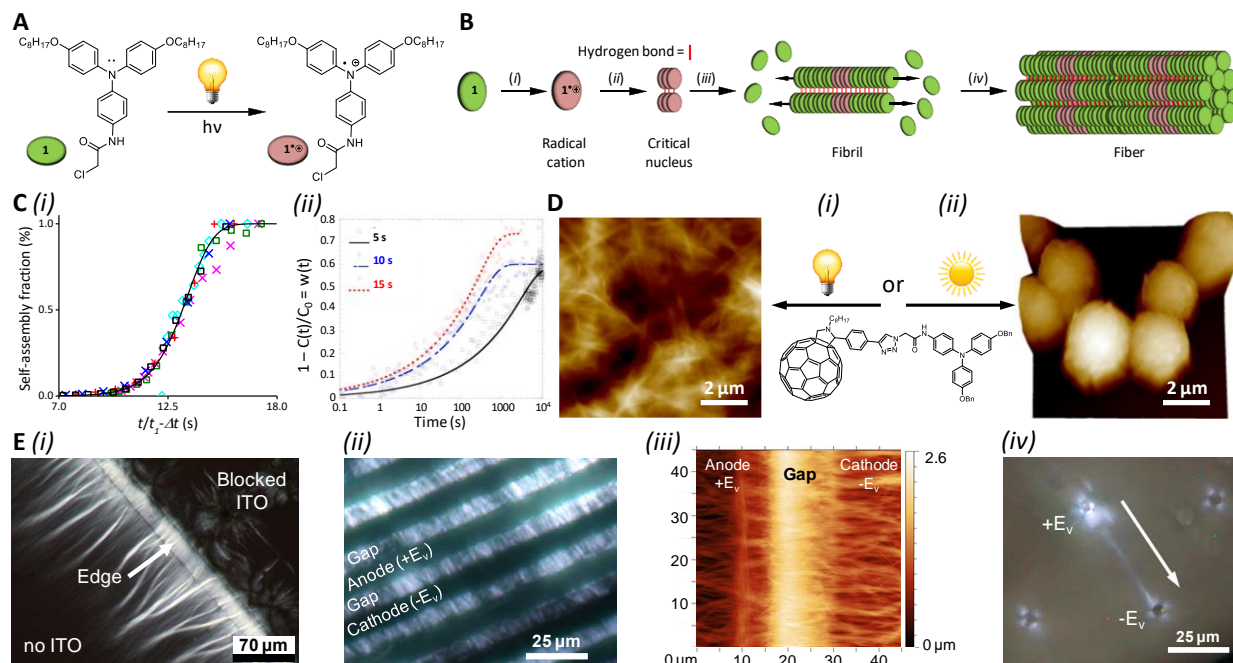


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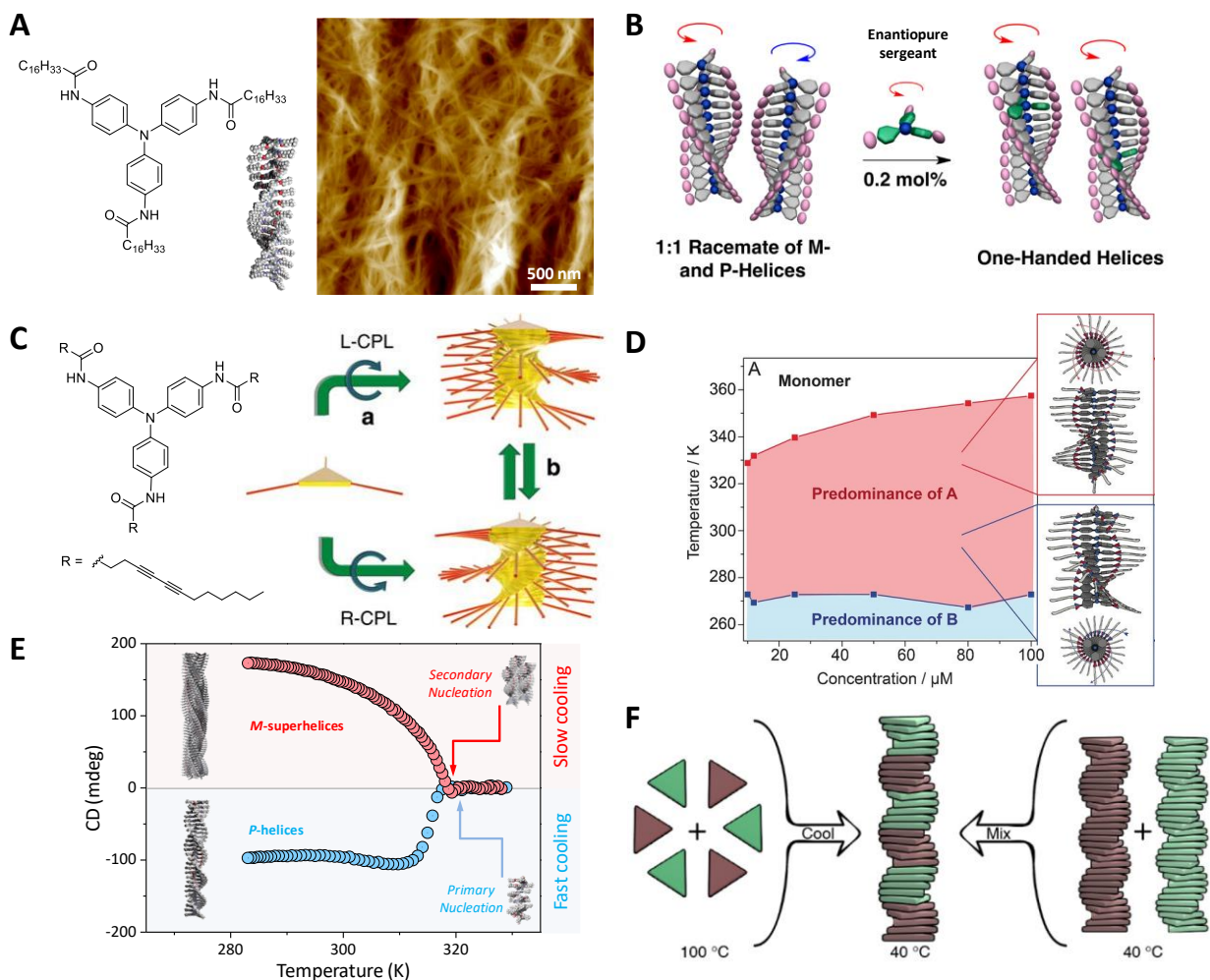
## FIGURES



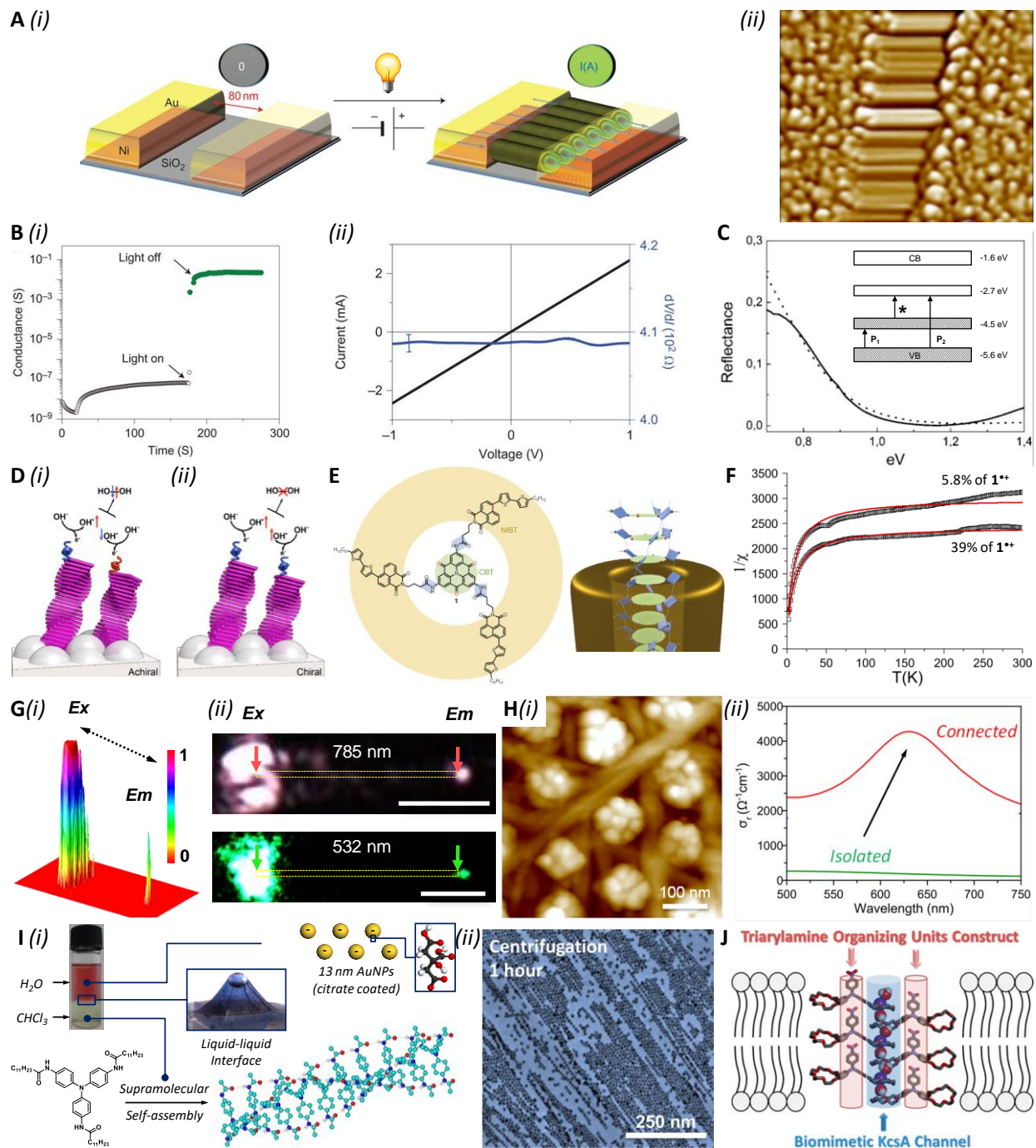
**Figure 1. Generic structures of triarylamine-based supramolecular polymers.** (A) Chiral propeller conformations of TPA ; (B) (i) « Snowflake », and (ii) « Mercedes-Benz » stacking conformations of TPA cores ; (C) (i) Typical mono-columnar helical stacking of TATA supramolecular polymers, and (ii) corresponding Atomic Force Microscopy (AFM) images; (D) XRD of TATA in a snowflake infinite network; (E) Double-columnar supramolecular stacks of TAA (i) top view, (ii) side view (arrows show  $\pi$ -stacking interactions), and (iii) corresponding AFM image; (F) Liquid-crystalline mesophase of columnar TAA; (G) AFM image of a 3D supramolecular polymer composed of fullerenes substituted by 12 TAA units.



**Figure 2. Supramolecular dynamics of triarylamine *mono*-amides.** (A) Oxidation of TAA to its radical cation; (B) Nucleation-growth polymerization mechanism starting from a catalytic oxidation of TAA; (C) (i) Universal nucleation growth master curve of TAA fibers upon catalytic oxidation, and (ii) Sigmoidal time-growth of TAA-based supramolecular polymers followed by light scattering; (D) AFM images of (i) white light and (ii) sunlight promoted self-assemblies of fullerene-TAA conjugates leading to ribbons and sphere, respectively; (E) (i) Electrochemically triggered nucleation growth of TAA polymers from solution at the edge of an ITO cell; (ii) Polarized optical microscopy (POM) image of interdigitated electrodes connected by supramolecular polymerization and (iii) corresponding AFM image; (iv) POM image of microarray electrodes connected by supramolecular polymerization.



**Figure 3. Supramolecular dynamics of triarylamine tris-amides.** (A) Typical gel made of racemic *M* and *P* TATA fibers imaged by AFM; (B) Sergeant and soldier chiral amplification of TATA fibers; (C) Chiral formation and inversion of TATA helices triggered by CPL; (D) Phase diagram showing helical inversion of TATA helices; (E) Sequential nucleation growth of TATA and bifurcation between *P*-helices and *M*-superhelices; (F) Supramolecular block copolymers made of TATA.



**Figure 4. Functional triarylamine-based supramolecular polymers.** (A) (i) Schematic device of the self-construction of TAA nanowires in between electrodes; (ii) corresponding AFM image; (B) (i) Conductance vs time during the self-construction process described in (A); and (ii) corresponding  $I/V$  curve at 4K; (C) Reflectance of a film made of doped TATA, and its

corresponding half-filled polaronic structure as inset; **(D)** (i) Racemic and (ii) one handed TATA-based spin filter used for water splitting; **(E)** Planar carbonyl-bridged TATA-based single fiber showing long-range exciton diffusion; **(F)** EPR visualization of temperature independent metallic electrons in TATA single crystals; **(G)** (i) Reconstructed excitation and emission of TATA-based waveguides shown in (ii) (bar scale = 4  $\mu\text{m}$ ); **(H)** (i) Hybrid film made of TATA nanowires connecting gold nanoparticles; and (ii) corresponding optical conductivity for the connected and non-connected devices; **(I)** (i) Supramolecular polymerization at liquid-liquid interface involving nanoparticles alignments (ii) ; **(J)** XRD structure of an artificial  $\text{K}^+$  channel made of TATA molecules in a phospholipid bilayer.

