A4: Light-triggered self-assemblies of triarylamine-based conjugates

A. Wolf
Supervisors: N. Giuseppone, S. Ludwigs

Presentations

- 4 oral IRTG
- 6 poster IRTG
- 1 poster others

Publications

[1] Busseron, E.; Cid, J.-J.; Wolf, A.; Du, G.; Moulin, E.; Fuks, G.; Maaloum, M.; Polavarapu, P.; Ruff, A.; Saur, A.-K.; Ludwigs, S.; Giuseppone, N. *ACS Nano* **2015**, *9*, 2760–2772.

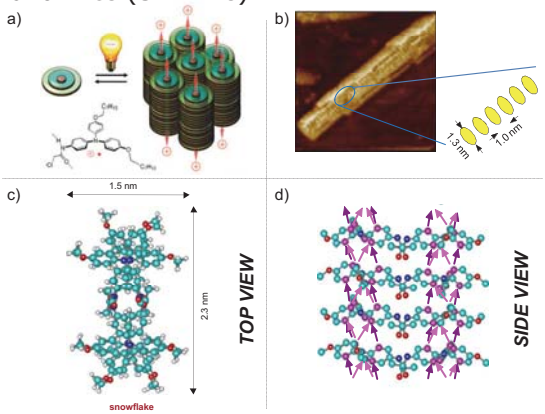
[2] Wolf, A.; Moulin, E.; Cid, J.-J.; Goujon, A.; Du, G.; Busseron, E.; Fuks, G.; Giuseppone, N. *Chem. Commun.* **2015**, *51*, 4212–4215.

Other activities

- ERC Meeting „Frontier Research in Chemistry" (November 22-24, 2012) in Strasbourg

Motivation

Self-assembly of supramolecular triarylamine nanowires (STANWs):

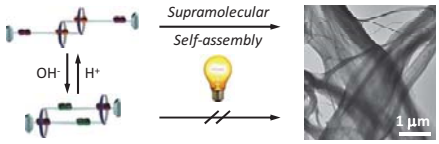


a-b) Visible light irradiation of triarylamine (TAA) solutions produces small amounts of radical cations which trigger the piling up with their neutral counterparts into one-dimensional TAA stacks. These stacks bundle into three-dimensional nanofibers that display metallic conductivity; c-d) Molecular arrangements of TAA in bicolumnar "snowflake" stacks determined by all-atomic modelling (conducting pathways are marked with violet arrows).

See *Angew. Chem. Int. Ed.* **2010**, *49*, 6974 and *ACS Nano* **2014**, *8*, 10111.

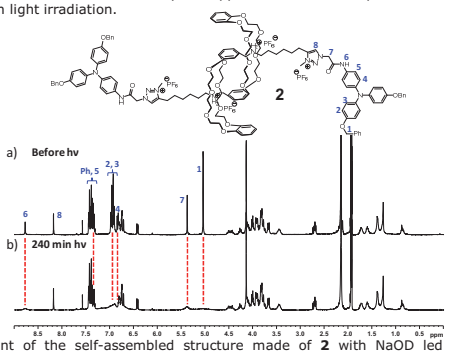
STANWs associated with a bistable [*c*2] daisy chain rotaxane – *dynamic*

A logic gate with INHIBIT function [2]:



A logic gate based on a bistable [*c*2] daisy chain rotaxane decorated with lateral triarylamine units is described, giving rise to an INHIBIT logic function using proton concentration and light as inputs, and producing dual color change and supramolecular self-assembly as outputs.

Upon light-irradiation of a solution of **2** (a, before irradiation; b, after irradiation), ^{1}H NMR signals arising from the triarylamine core disappear as a result of their anisotropic stacking and radical delocalization, thus evidencing the formation of supramolecular nanostructures (see TEM image above). This self-assembly process was also characterized by the appearance of an absorption band at 760 nm upon light irradiation.



Treatment of the self-assembled structure made of **2** with NaOD led to the reappearance of NMR signals corresponding to the triarylamine core, thus demonstrating the reversibility of the self-assembly upon deprotonation of the rotaxane unit.

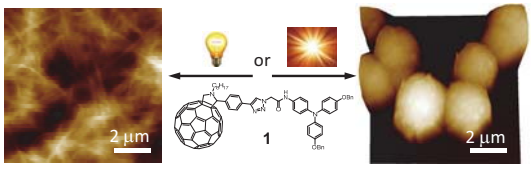
Truth table for **2**:

Input 1 (white light)	Input 2 (base)	Output 1 (760nm absorption)	Output 2 (self-assembly)
0	0	0	0
0	1	0	0
1	0	1	1
1	1	0	0

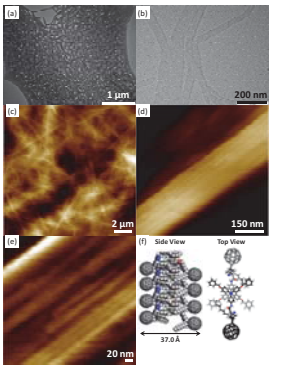
STANWs associated with [60]fullerenes – *static*

TAA-C_{60} donor-acceptor conjugates [1]:

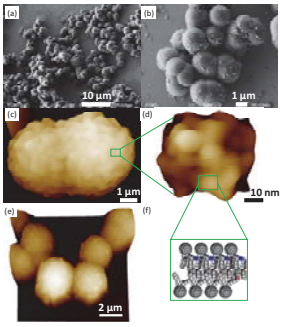
A family of triarylamine-fullerene conjugates capable of self-assembling into supramolecular nanostructures upon light-activation has been synthesized. In particular, for conjugate **1**, the nature of light (variation in intensity of UV photons) used to trigger the self-organization determines the nanostructuration of the self-assembly leading to either entangled fibers (halogen lamp, *left*) or monodisperse spherical aggregates (UV lamp, resp. sunlight, *right*).



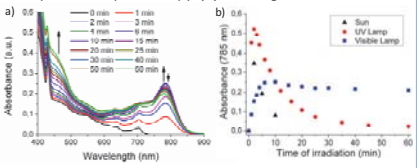
TEM (a, b) and AFM images (c-e) of **1** obtained from a $CHCl_3$ solution irradiated with white light and drop-casted on carbon-coated Cu grid (a,b) or spin-coated on mica surface (c-e); Molecular modeling by DFT of the TAA stacks of **1** (f).



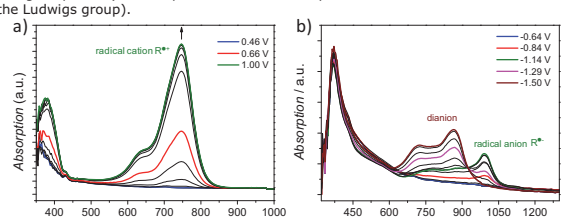
SEM (a, b) and AFM images (c-e) of **1** obtained from a $CHCl_3$ solution irradiated with sunlight (a, b) or UV-light (c–e) and drop-casted on Si wafer (a, b) or spin-coated on mica surface (c-e) ; Molecular modeling by DFT of the TAA stacks of **1** (f).



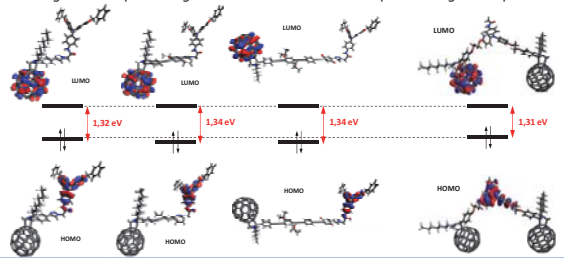
Self-assembly of **1** monitored by Vis-NIR spectroscopy (a) showing an increase of the absorbance at around 785 nm arising from radical cationic species and (b) evolution of this absorbance as a function of time of irradiation with different light sources (Sun,UV lamp and halogen lamp)



UV/Vis spectra recorded during a) the forward scan of the oxidation and b) the forward scan of the reduction of compound **1** revealing the formation of various charged species (*In-situ* spectroelectrochemistry results obtained in collaboration with the Ludwigs group).



DFT-calculated HOMO/LUMO frontier orbital schemes and $E_{gap,\ CV}$ values of TAA-C_{60} conjugates. All compounds have very low and narrow HOMO-LUMO gaps (<1.40 eV), promoting them as promising molecules for efficient ambipolar charge transport.



Conclusions & outlook

We demonstrated that STANWs can be attached to functional units to build more complex entities while retaining their light-triggered self-assembly properties.
In static conjugates, supramolecular heterojunctions can be formed and according to their low bandgaps (< 1.35 eV or lower), these donor-acceptor molecules might display ambipolar charge transport properties.
When STANWs were incorporated into dynamic pH-switchable molecular muscles, the combination of pH and light triggers allow the development of dual triggered systems. This led to new types functional systems that can operate as and INHIBIT logic gate via orthogonal external stimuli (pH and light).
Importantly, the fact that the self-assembly properties of STANWs remain intact in these systems is promising for further studies (see project C6 of Renewal Proposal).