- **Photo- and Thermoresponsive Supramolecular Assemblies: Reversible Photorelease of K’ions and Constitutional Dynamics**

  **Abstract:**

  Freed at the flick of a photoswitch: An acyl hydrazone forms supramolecular assemblies upon the binding of specific salts, such as potassium thiocyanate. This process presents cation and anion selectivity as well as thermo- and photoreversibility (see scheme). In particular, the system displays photorelease of potassium cations and undergoes dynamic component exchange in the acyl hydrazone.

- **Peptide-Directed Synthesis and Assembly of Hollow Spherical CoPt Nanoparticle Superstructures**

  **Abstract:**

  From "nano" to "super": Peptide conjugates that consist of cobalt-binding peptides terminated with tails of biphenyl units were used to direct the synthesis and assembly of hollow spherical superstructures of CoPt nanoparticles (see picture). These magnetically separable superstructures exhibit electrocatalytic activity for methanol oxidation.

- **Controlling Helix Formation in the γ-Peptide Superfamily: Heterogeneous Foldamers with Urea/Amide and Urea/Carbamate Backbones**

  **Abstract:**
One fold to rule them all: New heterogeneous aliphatic backbone foldamers belonging to the \( \gamma \)-peptide superfamily and containing various combinations of urea/amide (U/A) and urea/carbamate (U/C) units are reported. Structural studies at atomic resolution reveal hydrogen-bonded helical structures akin to that formed by cognate U, homooligomers.

- X-ray analysis on the nanogram to microgram scale using porous complexes

Abstract:

X-ray single-crystal diffraction (SCD) analysis has the intrinsic limitation that the target molecules must be obtained as single crystals. Here we report a protocol for SCD analysis that does not require the crystallization of the sample. In our method, tiny crystals of porous complexes are soaked in a solution of the target, such that the complexes can absorb the target molecules. Crystallographic analysis clearly determines the absorbed guest structures along with the host frameworks. Because the SCD analysis is carried out on only one tiny crystal of the complex, the required sample mass is of the nanogram–microgram order. We demonstrate that as little as about 80 nanograms of a sample is enough for the SCD analysis. In combination with high-performance liquid chromatography, our protocol allows the direct characterization of multiple fractions, establishing a prototypical means of liquid chromatography SCD analysis. Furthermore, we unambiguously determined the structure of a scarce marine natural product using only 5 micrograms of the compound.

- Steroid-based facial amphiphiles for stabilization and crystallization of membrane proteins

Abstract:
Amphiphile selection is a critical step for structural studies of membrane proteins (MPs). We have developed a family of steroid-based facial amphiphiles (FAs) that are structurally distinct from conventional detergents and previously developed FAs. The unique FAs stabilize MPs and form relatively small protein–detergent complexes (PDCs), a property considered favorable for MP crystallization. We attempted to crystallize several MPs belonging to different protein families, including the human gap junction channel protein connexin 26, the ATP binding cassette transporter MsBA, the seven-transmembrane G protein-coupled receptor-like bacteriorhodopsin, and cytochrome P450s (peripheral MPs). Using FAs alone or mixed with other detergents or lipids, we obtained 3D crystals of the above proteins suitable for X-ray crystallographic analysis. The fact that FAs enhance MP crystallizability compared with traditional detergents can be attributed to several properties, including increased protein stability, formation of small PDCs, decreased PDC surface flexibility, and potential to mediate crystal lattice contacts.

- A homogeneous transition metal complex for clean hydrogen production from methanol–water mixtures

  **Abstract:**

  The development of an efficient catalytic process that mimics the enzymatic function of alcohol dehydrogenase is critical for using biomass alcohols for both the production of H\textsubscript{2} as a chemical energy carrier and fine chemicals under waste-free conditions. Dehydrogenation of alcohol–water mixtures into their corresponding acids with molecular hydrogen as the sole by-product from the reaction can be catalysed by a ruthenium complex with a chelating bis(olefin) diazadiene ligand. This complex, \([\text{K(dme)}\,\,][\text{Ru(H)}(\text{trop}_2\text{dad})]\), stores up to two equivalents
of hydrogen intramolecularly, and catalyses the production of H₂ from alcohols in the presence of water and a base under homogeneous conditions. The conversion of a MeOH–H₂O mixture proceeds selectively to CO₂/H₂ gas formation under neutral conditions, thereby allowing the use of the entire hydrogen content (12% by weight). Isolation and characterization of the ruthenium complexes from these reactions suggested a mechanistic scenario in which the trop₂dad ligand behaves as a chemically ‘non-innocent’ co-operative ligand.

- Improving the hydrogen oxidation reaction rate by promotion of hydroxyl adsorption
  
  **Abstract:**

  The development of hydrogen-based energy sources as viable alternatives to fossil-fuel technologies has revolutionized clean energy production using fuel cells. However, to date, the slow rate of the hydrogen oxidation reaction (HOR) in alkaline environments has hindered advances in alkaline fuel cell systems. Here, we address this by studying the trends in the activity of the HOR in alkaline environments. We demonstrate that it can be enhanced more than fivefold compared to state-of-the-art platinum catalysts. The maximum activity is found for materials (Ir and Pt₀.₁Ru₀.₉) with an optimal balance between the active sites that are required for the adsorption/dissociation of H₂ and for the adsorption of hydroxyl species (OHₐd). We propose that the more oxophilic sites on Ir(defects) and PtRu material (Ru atoms) electrodes facilitate the adsorption of OHₐd species. Those then react with the hydrogen intermediates (Hₐd) that are adsorbed on more noble surface sites.

- Synthesis of Cylindrical Polymer Brushes with Umbrella-Like Side Chains via a Combination of Grafting-from and Grafting-onto Methods
  
  **Abstract:**

  Wormlike molecular brushes with dendritic terminals

  Cylindrical polymer brushes with umbrella-like side chains have been synthesized by a combination of grafting-from and grafting-onto methods. First, the polymer brushes with azido end-functionalized poly(tert-butyl acrylate) (PtBA-N₃) side chains, PBIEM-B-(PtBA-N₃), were prepared by atom transfer
radical polymerization (ATRP) of tBA monomers using polyinitiator PBIEM followed by a substitution of bromo-side terminals with sodium azide. Subsequently, polyamidoamino dendrons of three generations with a propargyl focal point (Gn) were introduced onto the brush-shaped PtBA-N\textsubscript{3} by copper-catalyzed azide–alkyne cycloaddition (CuAAC) coupling reaction. The efficiency of CuAAC between PtBA-N\textsubscript{3} side chains and Gn has showed a dependence on generation number n of the dendrons. At the feed ratio of [Gn]:[N\textsubscript{3}] = 1:1, the grafting efficiency of the first generation dendron (G1) reached above 95%, whereas that of G2 and G3 was at least 84% and 73%, respectively. AFM images indicated that diameter of the brushes hybridized with G3 increased obviously than that of the brushes without dendrons.

  
  **Abstract:**

The present study reports on the development of composite gold nanoparticles (AuNPs)/polymersome formulations, based on pH-responsive biocompatible polymer vesicles integrating prefunctionalized AuNPs, doped with a hydrophobic model probe for improved multimodal drug delivery. The polymer vesicles were prepared from an amphiphilic pentablock terpolymer poly(ɛ-caprolactone)-b-poly(ethylene oxide)-b-poly(2-vinylpyridine)-b-poly(ethylene oxide)-b-poly(ɛ-caprolactone) (PCL-PEO-P2VP-PEO-PCL), consisting of a pH-sensitive and biodegradable P2VP/PCL membrane, surrounded by neutral hydrophilic PEO looping chains. Additionally, partial quaternization of the P2VP block has been performed to introduce cationic moieties. Water-dispersible AuNPs carrying a hydrophobic molecule were encapsulated in the hydrophilic aqueous lumen of the vesicles, and the release was monitored at pH conditions simulating physiological and tumor environments. The complex delivery of the cargos from these vesicles showed improved and controlled kinetics relative to the individual nanocarriers, which could be further tuned by pH and chemical modification of the membrane forming block.

- **A facile “click” approach to functionalised metallo-supramolecular architectures** Lewis, J. E. M.; McAdam, C. J.; Gardiner, M. G.; Crowley, J. D. *Chem. Commun.* 2013, 49, 3398-3400.
  
  **Abstract:**

Herein we describe a CuAAC “click” methodology for exo-functionalisation of Pd2L4...
metallosupramolecular architectures. The potentially coordinating 1,2,3-triazole does not affect formation of the desired discrete complexes, nor does this external functional decoration affect the cisplatin-binding ability of the interior cavity of the assembly.

- Direct electrical single-molecule detection of DNA through electron transfer induced by hybridization
  Abstract:

  Single-stranded DNA was utilized as a probe tip for single-molecule DNA detection. Hybridization of the DNA tip and target DNA induces electron tunneling through the resulting DNA duplex. It is demonstrated that the DNA tip allows not only genetic detection but also discovery of single-nucleotide polymorphisms at the single-molecule level.

- DNAzyme-Based Probes for Telomerase Detection in Early-Stage Cancer Diagnosis
  Abstract:

  All’s well that ends well: A PCR-free, DNAzyme-based telomerase sensor is demonstrated. Duplex formation between the PbII-specific DNAzyme fragment and telomere primer results in efficient and specific cleavage of telomere target after telomerase elongation (see figure). Our single-molecule probe design allows a quantifiable detection range from 0.1–1 μg total protein from cancer-cell lysate. Human telomerase is a polymerase enzyme that adds tandem repeats of DNA (TTAGGG) in the telomeric region to the ends of chromosomes. Since telomerase can be detected in immortalized, but not normal, somatic cells, it has been considered a selective target for cancer chemotherapy. Here, we describe a DNAzyme-based probe to detect the presence of telomerase in cell lysates. Telomerase elongates the primer site on the probe. Subsequent addition of the PbII cofactor activates the
DNAzyme, which cleaves the elongated fragment at the RNA site, releasing the probe for repetitive cycling and signal amplification. The cleaved fragment is detected by a reporter molecular beacon. Enzymatic amplification with rapid turnover allows detection of telomerase in the range of 0.1 to 1 µg cell lysate, with a fivefold increase in signal level for cancer cells over normal cells. This probe design can provide a simple, yet rapid and sensitive, measurement of telomerase activity.

- **Molecular Spoked Wheels: Synthesis and Self-Assembly Studies on Rigid Nanoscale 2D Objects**
  **Abstract:**

  *The wheel deal:* By relying on an optimized modular synthesis, derivatives of a new molecular spoked-wheel structure were accessed on a several hundred milligram scale (see figure). The self-assembly behavior of these approximately 4 nm-sized nanodisks was also studied in detail by means of dynamic light scattering, small-angle X-ray scattering, and scanning tunneling microscopy. We present the efficient synthesis of a new molecular spoked-wheel structure (**MSW-3**). Two derivatives with diameters of approximately 4 nm have been prepared. By highlighting the importance of pseudo-high-dilution conditions during cyclization, we were able to access the compounds on a several hundred milligram scale. In addition to the standard characterization (NMR spectroscopy, MS), we describe a detailed investigation of the optical properties of the fluorescent MSWs by comparison with appropriate model chromophores. Furthermore, a comprehensive study of the structure in solution by means of light- and X-ray scattering experiments has been conducted. Scanning tunneling microscopy (STM) revealed the two-dimensional organization of the molecules on highly oriented pyrolytic graphite and emphasized the spoked-wheel structure. The diameter of these molecules measured by small-angle X-ray scattering is in very good agreement with that obtained from STM and matches the results of molecular modeling. This confirms the rigidifying effect of the spokes, which results in highly shape-persistent nanometer-sized oblate organic compounds.

- **Tuning supramolecular mechanics to guide neuron development**
  **Abstract:**
The mechanical properties of the extracellular matrix (ECM) are known to influence neuronal differentiation and maturation, though the mechanism by which neuronal cells respond to these biophysical cues is not completely understood. Here we design ECM mimics using self-assembled peptide nanofibers, in which fiber rigidity is tailored by supramolecular interactions, in order to investigate the relationship between matrix stiffness and morphological development of hippocampal neurons. We observe that development of neuronal polarity is accelerated on soft nanofiber substrates, and results from the dynamics of neuronal processes. While the total neurite outgrowth of non-polar neurons remains conserved, weaker adhesion of neurites to soft PA substrate facilitates easier retraction, thus enhancing the frequency of “extension-retraction” events. We hypothesize that higher neurite motility enhances the probability of one neurite to reach a critical length relative to others, thereby initiating the developmental sequence of axon differentiation. Our results suggest that substrate stiffness can influence neuronal development by regulating its dynamics, thus providing useful information on scaffold design for applications in neural regeneration.

- **Self-Assembly of Elastin–Mimetic Double Hydrophobic Polypeptides**
  **Abstract:**

We have constructed a novel class of “double-hydrophobic” block polypeptides based on the hydrophobic domains found in native elastin, an extracellular matrix protein responsible for the elasticity and resilience of tissues. The block polypeptides comprise proline-rich poly(VPGXG) and glycine-rich poly(VGGVG), both of which dehydrate at higher temperature but form distinct secondary structures, β-turn and β-sheet respectively. In water at 45 °C, the block polypeptides initially assemble into nanoparticles rich in β-turn structures, which further connect into long (>10
μm), beaded nanofibers along with the increase in the β-sheet content. The nanofibers obtained are well-dispersed in water, and show thermoresponsive properties. Polypeptides comprising each block component assemble into different morphologies, showing that the conjugation of poly(VPGXG) and poly(VGGVG) plays a role for beaded fiber formation. These results may provide innovative ideas for designing peptide-based materials but also opportunities for developing novel materials useful for tissue engineering and drug delivery systems.

- **Artificial Z-Scheme Constructed with a Supramolecular Metal Complex and Semiconductor for the Photocatalytic Reduction of CO₂**
  **Abstract:**

  A hybrid for the visible-light-driven photocatalytic reduction of CO₂ using methanol as a reducing agent was developed by combining two different types of photocatalysts: a Ru(II) dinuclear complex (RuBLRu) used for CO₂ reduction is adsorbed onto Ag-loaded TaON (Ag/TaON) for methanol oxidation. Isotope experiments clearly showed that this hybrid photocatalyst mainly produced HCOOH (TN = 41 for 9 h irradiation) from CO₂ and HCHO from methanol. Therefore, it converted light energy into chemical energy (ΔG° = +83.0 kJ/mol). Photocatalytic reaction proceeds by the stepwise excitation of Ag/TaON and the Ru dinuclear complex on Ag/TaON, similar to the photosynthesis Z-scheme.

- **Direct Measurement of Electron Transfer through a Hydrogen Bond between Single Molecules**
  **Abstract:**

  Understanding electron transfer (ET) from a single molecule to another single molecule holds essential importance to realize bottom-up molecular devices in which constituent molecules are self-assembled via noncovalent interactions between each other. However, rather little is currently known
about the ET properties at the single-molecule interface. Here we employ molecular tips to quantify the ET through a H-bond between single molecules. We found that a H-bond conducts electrons better than a covalent σ bond at short-range. Its conductance, however, decays steeply as the chain length of the H-bonded molecules increases. First-principle calculations were performed to reveal the electronic origin of the facile ET through the H-bond. Our results demonstrate that H-bonding in a molecular junction significantly affects its transport property.

- **Photoclickable Dendritic Molecular Glue: Noncovalent-to-Covalent Photochemical Transformation of Protein Hybrids**
  **Abstract:**
  A water-soluble dendron with a fluorescein isothiocyanate (FITC) fluorescent label and bearing nine pendant guanidinium ion (Gu+)/benzophenone (BP) pairs at its periphery (GlueBP-FITC) serves as a “photoclickable molecular glue”. By multivalent salt-bridge formation between Gu+ ions and oxyanions, GlueBP-FITC temporarily adheres to a kinesin/microtubule hybrid. Upon subsequent exposure to UV light, this noncovalent binding is made permanent via a cross-linking reaction mediated by carbon radicals derived from the photoexcited BP units. This temporal-to-permanent transformation by light occurs quickly and efficiently in this preorganized state, allowing the movements of microtubules on a kinesin-coated glass plate to be photochemically controlled. A fundamental difference between such temporal and permanent bindings was visualized by the use of “optical tweezers”.

- **A Supramolecular Janus Hyperbranched Polymer and Its Photoresponsive Self-Assembly of Vesicles with Narrow Size Distribution**
  **Abstract:**
  Herein, we report a novel Janus particle and supramolecular block copolymer consisting of two chemically distinct hyperbranched polymers, which is coined as Janus hyperbranched polymer. It is constructed by the noncovalent coupling between a hydrophobic hyperbranched poly(3-ethyl-3-oxetanemethanol) with an apex of an azobenzene (AZO) group and a hydrophilic hyperbranched...
polyglycerol with an apex of a β-cyclodextrin (CD) group through the specific AZO/CD host–guest interactions. Such an amphiphilic supramolecular polymer resembles a tree together with its root very well in the architecture and can further self-assemble into unilamellar bilayer vesicles with narrow size distribution, which disassembles reversibly under the irradiation of UV light due to the trans-to-cis isomerization of the AZO groups. In addition, the obtained vesicles could further aggregate into colloidal crystal-like close-packed arrays under freeze-drying conditions. The dynamics and mechanism for the self-assembly of vesicles as well as the bilayer structure have been disclosed by a dissipative particle dynamics simulation.

- A triphenylamine-based four-armed molecule for solution-processed organic solar cells with high photo-voltage
  Abstract:
  A new four-armed molecule Th₄(DTPAB) with a triphenylamine–benzothiadiazole–triphenylamine unit as the core and 4-hexylthiophene as arms was synthesized. Solution-processed organic solar cells based on blends of Th₄(DTPAB) and PC₇₁BM demonstrate a power conversion efficiency of 3.18% with a high open circuit voltage of 0.96 V.

- Advanced materials for solid-state refrigeration
  Abstract:
  Recent progress on caloric effects are reviewed. The application of external stimuli such as magnetic field, hydrostatic pressure, uniaxial stress and electric field give rise respectively to magnetocaloric, barocaloric, elastocaloric and electrocaloric effects. The values of the relevant quantities such as isothermal entropy and adiabatic temperature-changes are compiled for selected materials. Large values for these quantities are found when the material is in the vicinity of a phase transition. Quite
often there is coupling between different degrees of freedom, and the material can exhibit cross-
response to different external fields. In this case, the material can exhibit either conventional or
inverse caloric effects when a field is applied. The values reported for the many caloric effects at
moderate fields are large enough to envisage future application of these materials in efficient and
environmental friendly refrigeration.

- Highly Transparent and Flexible Nanopaper Transistors
  Abstract:

Renewable and clean “green” electronics based on paper substrates is an emerging field with
intensifying research and commercial interests, as the technology combines the unique properties of
flexibility, cost efficiency, recyclability, and renewability with the lightweight nature of paper. Because
of its excellent optical transmittance and low surface roughness, nanopaper can host many types of
electronics that are not possible on regular paper. However, there can be tremendous challenges with
integrating devices on nanopaper due to its shape stability during processing. Here we demonstrate
for the first time that flexible organic field-effect transistors (OFETs) with high transparency can be
fabricated on tailored nanopapers. Useful electrical characteristics and an excellent mechanical
flexibility were observed. It is believed that the large binding energy between polymer dielectric and
cellulose nanopaper, and the effective stress release from the fibrous substrate promote these
beneficial properties. Only a 10% decrease in mobility was observed when the nanopaper transistors
were bent and folded. The nanopaper transistor also showed excellent optical transmittance up to
83.5%. The device configuration can transform many semiconductor materials for use in flexible
green electronics.

- Nanotools for Neuroscience and Brain Activity Mapping
  Alivisatos, A. P.; Andrews, A. M.; Boyden, E. S.; Chun, M.; Church, G. M.; Deisseroth, K.;
  Donoghue, J. P.; Fraser, S. E.; Lippincott-Schwartz, J.; Looger, L. L.; Masmanidis, S.; McEuen, P.
  L.; Nurmiakko, A. V.; Park, H.; Peterka, D. S.; Reid, C.; Roukes, M. L.; Scherer, A.; Schnitzer, M.;
  ACS Nano 2013, 7, 1850-1866.
  Abstract:

Neuroscience is at a crossroads. Great effort is being invested into deciphering specific neural
interactions and circuits. At the same time, there exist few general theories or principles that explain
brain function. We attribute this disparity, in part, to limitations in current methodologies. Traditional neurophysiological approaches record the activities of one neuron or a few neurons at a time. Neurochemical approaches focus on single neurotransmitters. Yet, there is an increasing realization that neural circuits operate at emergent levels, where the interactions between hundreds or thousands of neurons, utilizing multiple chemical transmitters, generate functional states. Brains function at the nanoscale, so tools to study brains must ultimately operate at this scale, as well. Nanoscience and nanotechnology are poised to provide a rich toolkit of novel methods to explore brain function by enabling simultaneous measurement and manipulation of activity of thousands or even millions of neurons. We and others refer to this goal as the Brain Activity Mapping Project. In this Nano Focus, we discuss how recent developments in nanoscale analysis tools and in the design and synthesis of nanomaterials have generated optical, electrical, and chemical methods that can readily be adapted for use in neuroscience. These approaches represent exciting areas of technical development and research. Moreover, unique opportunities exist for nanoscientists, nanotechnologists, and other physical scientists and engineers to contribute to tackling the challenging problems involved in understanding the fundamentals of brain function.

- Synthesis and Properties of Naphthobisbenzo thiophene Diimides
  **Abstract:**

Laterally extended naphthalene diimides composed of naphthobisbenzo thiophene skeleton and two imide groups were synthesized, which exhibit interesting packing arrangements and optoelectrical properties.

- Photochemical Reaction Containers as Energy and Electron-Transfer Agents
  **Abstract:**

Two deep cavity cavitands, octa acid and resorcinol-capped octa acid, have been established to be good triplet energy donors in the excited state and electron donors in the ground state to excited acceptors. This property endows them the capacity to be “active” reaction containers. The above
recognition provides opportunities to investigate the excited state chemistry of host-encapsulated guests without the use of secondary triplet energy and electron donors.

- **Self-Assembly of a Bipolar Model of Biomacromolecules**

  **Abstract:**

  Extending recent work on a generic bipolar model proposed to study the nanochain formation of amelogenin molecules, we conduct a systematic investigation in this paper on the self-assembly of such a model via sweeping the relative parameter space. The bipolar model consists of a short-range attraction and an off-center Coulomb repulsion for the supermolecule. Through the Brownian dynamics simulation of both translational and rotational motions, we study the kinetics of the self-assembly and the structure of clusters formed within the system for various interaction settings. From the results of structure factor and cluster analysis, we find that the range of the repulsive interaction has a sensitive impact in controlling the cluster size, while the strength of the attractive interaction dominates the cluster morphology such that the greater the attraction among particles, the more elongated the cluster formed.

- **Effect of Sequence on the Ionization Behavior of a Series of Amphiphilic Polypeptides**

  **Abstract:**

  The behavior of five polypeptides made of hydrophilic and pH-responsive aspartic acid (Asp) and hydrophobic phenylalanine (Phe), which had been prepared by stitching together short well-defined sequences of Asp and Phe, was studied as a function of pH. The effect of pH on these polypeptides referred to as (Asp3Phe1)n, (Asp2Phe1)n, (Asp1Phe1)n, (Asp1Phe2)n, and (Asp1Phe3)n varied dramatically depending on their constituting sequence. The more hydrophobic polypeptides (Asp1Phe2)n and (Asp1Phe3)n behaved as if the Asp’s were isolated from each other and showed an apparent pKa (pKapp) that remained constant with level of ionization (α = [Asp–]/[Asp]total) and equaled 5.4 and 6.4, respectively. The more hydrophilic polypeptides (Asp3Phe1)n and (Asp2Phe1)n
behaved like weak polyacids showing a linear increase in pKaapp with increasing α. The pKaapp of (Asp1Phe1)n showed a trend as a function of α intermediate between the Asp-rich and Phe-rich polypeptides, behaving as if the Asp’s were isolated at low α values (<0.35) but acting as a weak polyacid for large α values (>0.35). The effect that α, and thus the charge density of the polypeptides, had on the collapse and aggregation of the polypeptides was characterized by conducting static light scattering and fluorescence measurements. Static light scattering measurements demonstrated that all polypeptides precipitated and aggregated in solution at a critical charge density of 0.2. Fluorescence measurements with pyrene indicated that this behavior was due to the formation of Phe aggregates in water. Together, these experiments provide a complete description of how pH affects the behavior of a series of unique amphiphilic polypeptides designed with a well-defined sequence.

- Hierarchical aggregation mechanism in heat-set metallosupramolecular gels using a tritopic functional ligand exhibiting temperature-triggered cis-to-trans molecular conversions
  Abstract:

We present the aggregation mechanism in a novel class of heat-set metallosupramolecular Ni₂BTC gels formed by complexation of a bis-terpyridine-cyclam (BTC), a tritopic ligand, with nickel ions (II). Viscosimetry, rheology, small-angle X-ray scattering, dynamic light scattering and impedance spectroscopy measurements are used to investigate the aggregative properties. Gels are obtained by heating the homogeneous solutions (Ni₂BTC in dimethylformamide) from room temperature to 50 °C for 24 hours, which is a remarkable phenomenology in the class of organic molecular gels. The hierarchical aggregation mechanism relies on a temperature-triggered cis-to-trans molecular conversion of the tritopic ligand at the central cyclam unit. At the nanoscale, the expansion of the coil-like species in the liquid phase to rodcoils allows, beyond a critical concentration, their percolation into transient gel networks. The use of such tritopic ligands gives access to homo- or hetero-metallogels that adapt their properties to the environmental conditions (temperature, pH, mechanical stress and applied electrical potential). Various molecular adjustment parameters (metal ions, metal sequence, metal–ligand stoichiometry, cyclam substituents) can be used to tune the aggregative properties of the system.

- Implications of macromolecular crowding for protein-protein association kinetics in the cytoplasm of living cells
  Abstract: