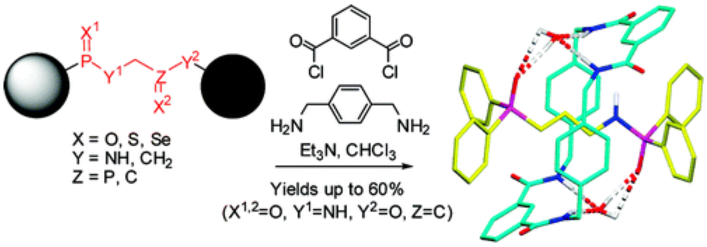
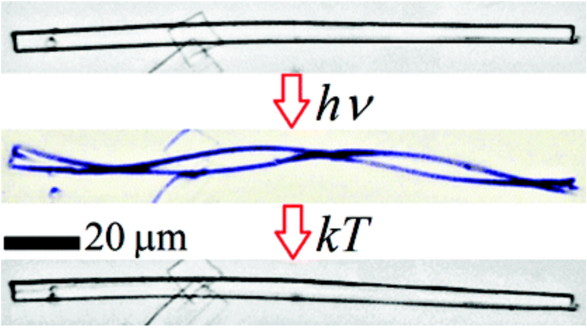
- Phosphorus-Based Functional Groups as Hydrogen Bonding Templates for Rotaxane Formation
  Ahmed, R.; Altieri, A.; D'Souza, D. M.; Leigh, D. A.; Mullen, K. M.; Papmeyer, M.; Slawin, A. M. Z.; Wong, J. K. Y.; Woollins, J. D. *J. Am. Chem. Soc.* **2011**, *133*, 12304–12310.
  Abstract:



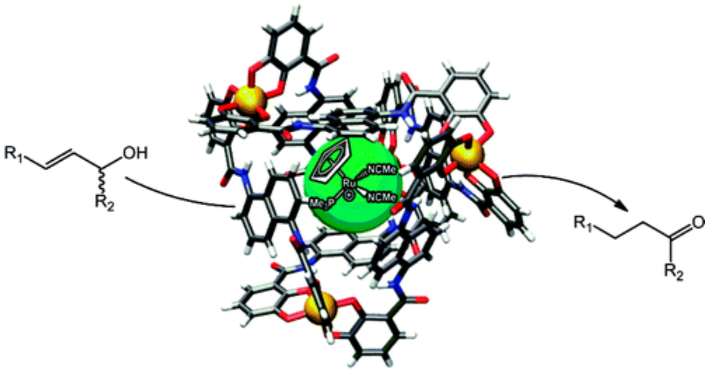
We report on the use of the hydrogen bond acceptor properties of some phosphorus-containing functional groups for the assembly of a series of [2]rotaxanes. Phosphinamides, and the homologous thio– and selenophosphinamides, act as hydrogen bond acceptors that, in conjunction with an appropriately positioned amide group on the thread, direct the assembly of amide-based macrocycles around the axle to form rotaxanes in up to 60% yields. Employing solely phosphorus-based functional groups as the hydrogen bond accepting groups on the thread, a *bis*(phosphinamide) template and a phosphine oxide–phosphinamide template afforded the corresponding rotaxanes in 18 and 15% yields, respectively. X-ray crystallography of the rotaxanes shows the presence of up to four intercomponent hydrogen bonds between the amide groups of the macrocycle and various hydrogen bond accepting groups on the thread, including rare examples of amide-to-phosphinamide, -thiophosphinamide, and -selenophosphinamide groups. With a phosphine oxide–phosphinamide thread, the solid-state structure of the rotaxane is remarkable, featuring no direct intercomponent hydrogen bonds but rather a hydrogen bond network involving water molecules that bridge the H-bonding groups of the macrocycle and thread through bifurcated hydrogen bonds. The incorporation of phosphorus-based functional groups into rotaxanes may prove useful for the development of molecular shuttles in which the macrocycle can be used to hinder or expose binding ligating sites for metal-based catalysts.

- Reversible Photoinduced Twisting of Molecular Crystal Microribbons
  Zhu, L.; Al-Kaysi, R. O.; Bardeen, C. J. *J. Am. Chem. Soc.* **2011**, *133*, 12569–12575.
  Abstract:



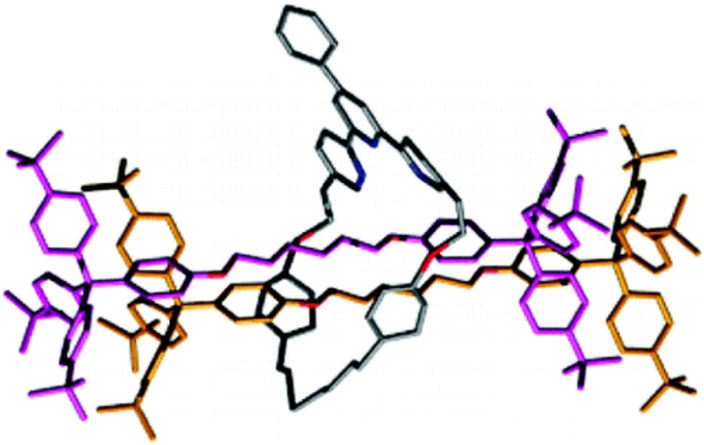
9-Anthracenecarboxylic acid, a molecule that undergoes a reversible [4 + 4] photodimerization, is prepared in the form of oriented crystalline microribbons. When exposed to spatially uniform light irradiation, these photoreactive ribbons rapidly twist. After the light is turned off, they relax back to their original shape over the course of minutes. This photoinduced motion can be repeated for multiple cycles. The final twist period and cross-sectional dimensions of individual microribbons are measured using a combination of atomic force and optical microscopies. Analysis of this data suggests that the reversible twisting involves the generation of interfacial strain within the ribbons between unreacted monomer and photoreacted dimer regions, with an interaction energy on the order of 3.4 kJ/mol. The demonstration of reversible twisting without the need for specialized irradiation conditions represents a new type of photoinduced motion in molecular crystals and may provide new modes of operation for photomechanical actuators.

- High-Turnover Supramolecular Catalysis by a Protected Ruthenium(II) Complex in Aqueous Solution
  Brown, C. J.; Miller, G. M.; Johnson, M. W.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc* **2011**, *133*, 11964–11966.
  Abstract:



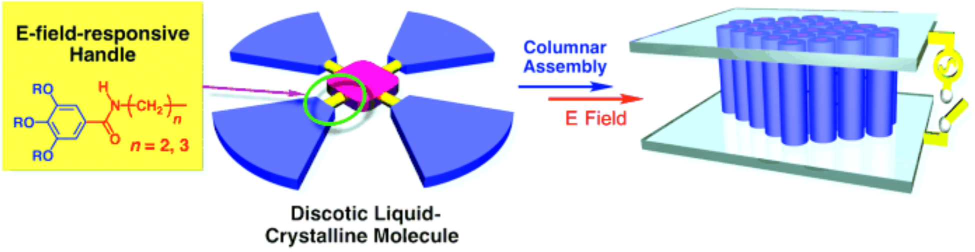
The design of a supramolecular catalyst capable of high-turnover catalysis is reported. A ruthenium(II) catalyst is incorporated into a water-soluble supramolecular assembly, imparting the ability to catalyze allyl alcohol isomerization. The catalyst is protected from decomposition by sequestration inside the host but retains its catalytic activity with scope governed by confinement within the host. This host–guest complex is a uniquely active supramolecular catalyst, capable of >1000 turnovers.

- En Route to a Molecular Sheaf: Active Metal Template Synthesis of a [3]Rotaxane with Two Axles Threaded through One Ring
  Cheng, H. M.; Leigh, D. A.; Maffei, F.; McGonigal, P. R.; Slawin, A. M. Z.; Wu, J. *J. Am. Chem. Soc.* **2011**, 133, 12298–12303.
  Abstract:



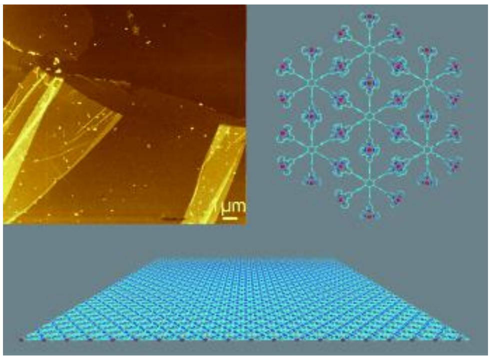
We report that a 2,2′:6′,2″-terpyridylmacrocycle–Ni complex can efficiently mediate the threading of two alkyl chains with bulky end groups in an active metal template sp3-carbon-to-sp3-carbon homocoupling reaction, resulting in a rare example of a doubly threaded [3]rotaxane in up to 51% yield. The unusual architecture is confirmed by X-ray crystallography (the first time that a one-ring-two-thread [3]rotaxane has been characterized in the solid state) and is found to be stable with respect to dethreading despite the large ring size of the macrocycle. Through such active template reactions, in principle, a macrocycle should be able to assemble as many axles in its cavity as the size of the ring and the stoppers will allow. A general method for threading multiple axles through a macrocycle adds significantly to the tools available for the synthesis of different types of rotaxane architectures.

- Electric-Field-Responsive Handle for Large-Area Orientation of Discotic Liquid-Crystalline Molecules in Millimeter-Thick Films
  Miyajima, D.; Araoka, F.; Takezoe, H.; Kim, J.; Kato, K.; Takata, M.; Aida, T. *Angew. Chem. Int. Ed.* **2011**, *50*, 7865–7869.
  Abstract:



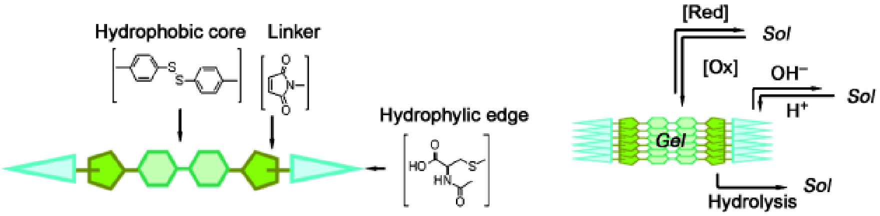
Current events: An electric-field-responsive handle (see picture) was developed that enables large-area and millimeter-thick unidirectional orientation of columnarly assembled π-conjugated liquid-crystalline molecules. The handles in the columns are hydrogen-bonded and align along the direction of an applied electric field.

- Synthesis of Free-Standing, Monolayered Organometallic Sheets at the Air/Water Interface
  Bauer, T.; Zheng, Z.; Renn, A.; Enning, R.; Stemmer, A.; Sakamoto, J.; Schlüter, A. D. *Angew. Chem. Int. Ed.* **2011**, *50*, 7879–7884.
  Abstract:



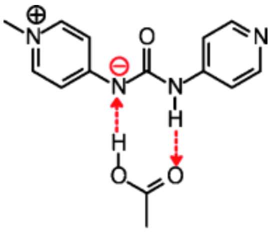
Sheets and rational synthesis are not like fire and water! Hexafunctional terpyridine monomers can be laterally connected by metal salts to result in a mechanically stable, sheetlike entity that can be transferred from the air/water interface to a solid substrate (see the folded, ca. 1.4 nm thin film) and spanned over micrometer-sized holes. This result is considered an important step on the way to 2D polymers.

- Versatile Low-Molecular-Weight Hydrogelators: Achieving Multiresponsiveness through a Modular Design
  Milanesi, L.; Hunter, C. A.; Tzokova, N.; Waltho, J. P.; Tomas, S. *Chem. Eur. J.* **2011**, *17*, 9753–9761.
  Abstract:



Multiresponsive low-molecular-weight hydrogelators (LMWHs) are ideal candidates for the development of smart, soft, nanotechnology materials. The synthesis is however very challenging. On the one hand, de novo design is hampered by our limited ability to predict the assembly of small molecules in water. On the other hand, modification of pre-existing LMWHs is limited by the number of different stimuli-sensitive chemical moieties that can be introduced into a small molecule without seriously disrupting the ability to gelate water. Herein we report the synthesis and characterization of multistimuli LMWHs, based on a modular design, composed of a hydrophobic, disulfide, aromatic moiety, a maleimide linker, and a hydrophilic section based on an amino acid, here *N*-acetyl-L-cysteine (NAC). As most LMWHs, these gelators experience reversible gel-to-sol transition following temperature changes. Additionally, the NAC moiety allows reversible control of the assembly of the gel by pH changes. The reduction of the aromatic disulfide triggers a gel-to-sol transition that, depending on the design of the particular LMWH, can be reverted by reoxidation of the resulting thiol. Finally, the hydrolysis of the cyclic imide moieties provides an additional trigger for the gel-to-sol transition with a timescale that is appropriate for use in drug-delivery applications. The efficient response to the multiple external stimuli, coupled to the modular design makes these LMWHs an excellent starting point for the development of smart nanomaterials with applications that include controlled drug release. These hydrogelators, which were discovered by serendipity rather than design, suggest nonetheless a general strategy for the introduction of multiple stimuli-sensitive chemical moieties, to offset the introduction of hydrophilic moieties with additional hydrophobic ones, in order to minimize the upsetting of the critical hydrophobic–hydrophilic balance of the LMWH.

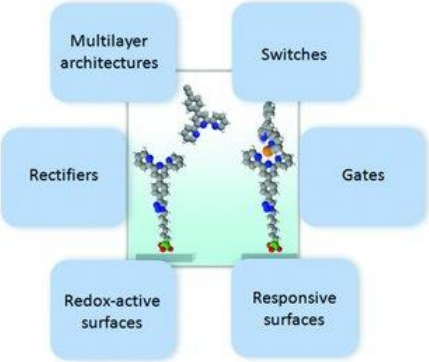
- Moderate and Advanced Intramolecular Proton Transfer in Urea–Anion Hydrogen-Bonded Complexes
  Baggi, G.; Boiocchi, M.; Fabbrizzi, L.; Mosca, L. *Chem. Eur. J.* **2011**, *17*, 9423–9439.
  Abstract:



[L···HX]

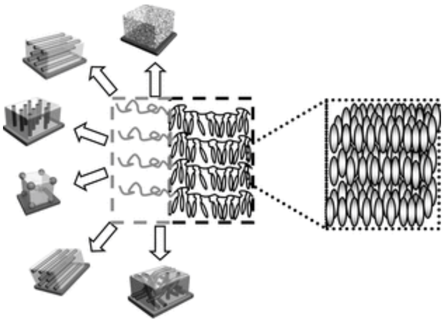
The study of the interactions of the three urea-based receptors **AH**, **BH**$^+$ and **CH**$^{2+}$ with a variety of anions, in MeCN, has made it possible to verify the current view that hydrogen bonding is frozen proton transfer from the donor (the urea N—H fragment in this case) to the acceptor (the anion X$^-$). The poorly acidic, neutral receptor **AH** establishes two equivalent hydrogen bonds N—H···X$^-$, with all anions, including CH_3COO^- and F$^-$, in which moderate proton transfer from N—H to the anion takes place. The strongly acidic, dicationic receptor **CH**$^{2+}$ forms, with most anions, complexes in which two inequivalent hydrogen bonds are present: one involving moderate proton transfer (N—H···X$^-$) and one in which advanced proton transfer has taken place, described as N$^-$···H—X. The degree of proton advancement is directly related to the basic tendencies of the anion. The cationic receptor **BH**$^+$ of intermediate acidic properties only forms complexes with two inequivalent hydrogen bonds (moderate+advanced proton transfer) with CH_3COO^- and F$^-$, and complexes with two equivalent hydrogen bonds (moderate proton transfer) with all the other anions. Moreover, [**B**···HF] and [**C**···HF]$^+$, on addition of a second F$^-$ ion, lose the bound HF molecule to give HF_2^-. Release of CH_3COOH, with the formation of [CH_3COOH···CH_3COO]$^-$, also takes place with the [**B**···CH_3COOH] complex in the presence of a large excess of anion.

- Terpyridine-Functionalized Surfaces: Redox-Active, Switchable, and Electroactive Nanoarchitecturesgland
  Winter, A.; Hoeppener, S.; Newkome, G. R.; Schubert, U. S. *Adv. Mater.* **2011**, *23*, 3484–3498.
  Abstract:



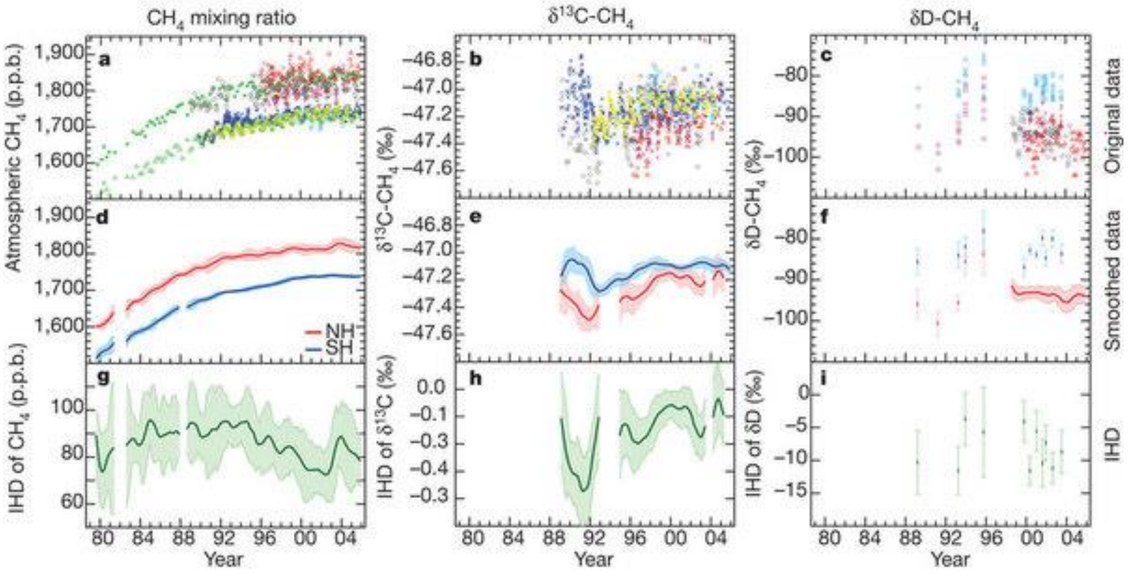
Terpyridines represent versatile functional supramolecular building blocks that are easily integrated in numerous devices and can readily modify surfaces. In particular, redox-active complexes with terpyridine ligands have been attached to surfaces, either by covalent or non-covalent interactions, and form highly ordered mono- or multilayer systems, since electronic and charge transport properties are major topics of interest. Their applications in nanoelectronics are a driving force for understanding and enabling the utilization of the supramolecular properties of terpyridines for surface modification. This area of research has received increasing attention during the last decade leading into the supramacromolecular regime. This Progress Report presents an overview of the state-of-the-art of surface modifications utilizing terpyridine systems and highlights main results, as well as modern trends, in this research area.

- Liquid-Crystalline Ordering Helps Block Copolymer Self-Assembly
  Yu, H.; Kobayashi, T.; Yang, H. *Adv. Mater.* **2011**, *23*, 3337–3344.
  Abstract:



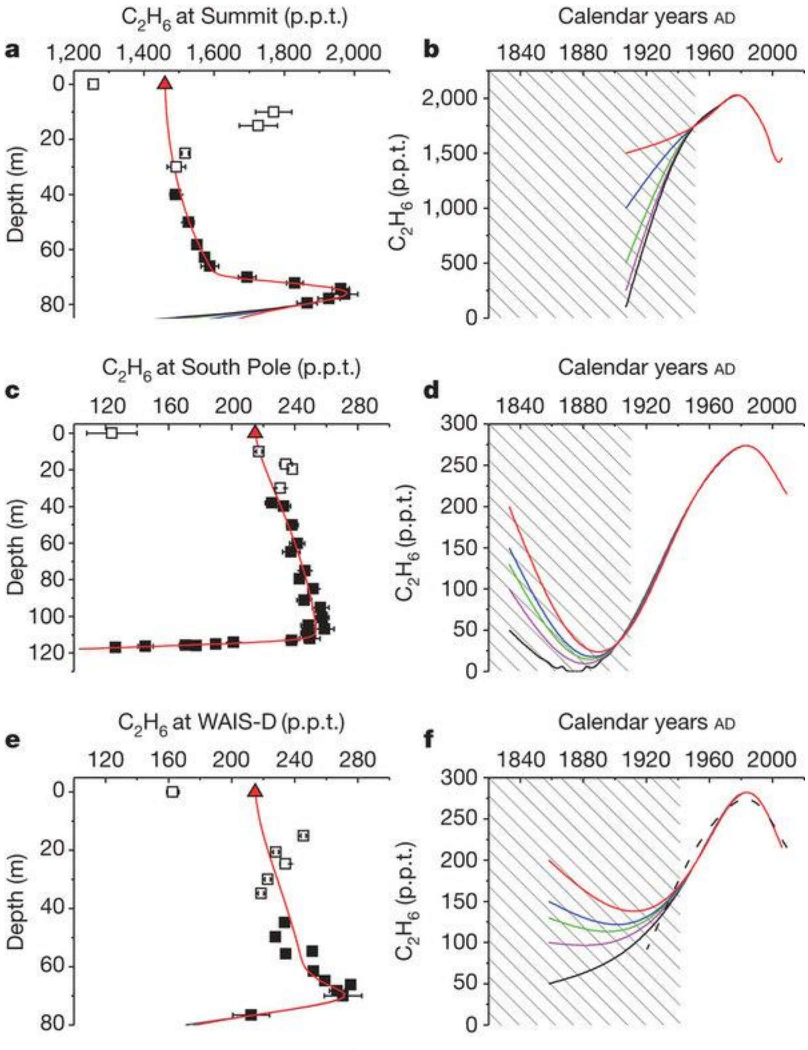
Interaction between liquid-crystalline elastic deformation and microphase separation in liquid-crystalline block copolymers enables them to supramolecularly assemble into ordered nanostructures with high regularity. With the help of liquid-crystalline alignment, parallel and perpendicular patterning of nanostructures is fabricated with excellent reproducibility and mass production, which provides nanotemplates and nanofabrication processes for preparing varieties of nanomaterials. Furthermore, nanoscale microphase separation improves the optical performance of block-copolymer films by eliminating the scattering of visible light, leading to advanced applications in optical devices and actuators. Recent progress in liquid-crystalline block copolymers, including their phase diagram, structure-property relationship, nanostructure control and nanotemplate applications, is reviewed.

- Reduced methane growth rate explained by decreased Northern Hemisphere microbial sources
  Kai, F. M.; Tyler, S. C.; Randerson, J. T.; Blake, D. R. *Nature* **2011**, *476*, 194-197.
  Abstract:



Atmospheric methane (CH_4) increased through much of the twentieth century, but this trend gradually weakened until a stable state was temporarily reached around the turn of the millennium, after which levels increased once more. The reasons for the slowdown are incompletely understood, with past work identifying changes in fossil fuel, wetland and agricultural sources and hydroxyl (OH) sinks as important causal factors. Here we show that the late-twentieth-century changes in the CH_4 growth rates are best explained by reduced microbial sources in the Northern Hemisphere. Our results, based on synchronous time series of atmospheric CH_4 mixing and $^{13}C/^{12}C$ ratios and a two-box atmospheric model, indicate that the evolution of the mixing ratio requires no significant change in Southern Hemisphere sources between 1984 and 2005. Observed changes in the interhemispheric difference of ^{13}C effectively exclude reduced fossil fuel emissions as the primary cause of the slowdown. The ^{13}C observations are consistent with long-term reductions in agricultural emissions or another microbial source within the Northern Hemisphere. Approximately half (51±18%) of the decrease in Northern Hemisphere CH_4 emissions can be explained by reduced emissions from rice agriculture in Asia over the past three decades associated with increases in fertilizer application and reductions in water use.

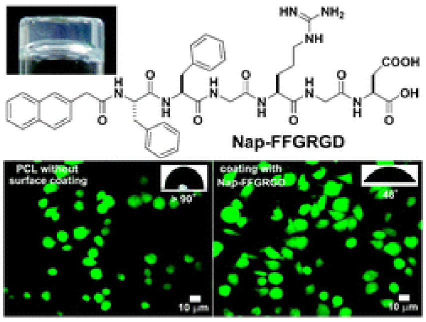
- Recent decreases in fossil-fuel emissions of ethane and methane derived from firn air
  Aydin, M.; Verhulst, K. R.; Saltzman, E. S.; Battle, M. O.; Montzka, S. A.; Blake, D. R.; Tang, Q.; Prather, M. J. *Nature* **2011**, *476*, 198-201.
  Abstract:



Methane and ethane are the most abundant hydrocarbons in the atmosphere and they affect both atmospheric chemistry and climate. Both gases are emitted from fossil fuels and biomass burning, whereas methane (CH_4) alone has large sources from wetlands, agriculture, landfills and waste water. Here we use measurements in firn (perennial snowpack) air from Greenland and Antarctica to reconstruct the atmospheric variability of ethane (C_2H_6) during the twentieth century. Ethane levels rose from early in the century until the 1980s, when the trend reversed, with a period of decline over the next 20 years. We find that this variability was primarily driven by changes in ethane emissions from fossil fuels; these emissions peaked in the 1960s and 1970s at 14–16 teragrams per year (1 Tg =

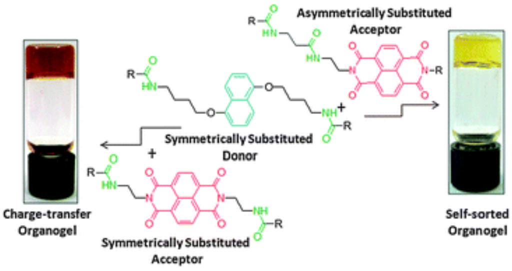
10^{12} g) and dropped to 8–10 Tg yr^{-1} by the turn of the century. The reduction in fossil-fuel sources is probably related to changes in light hydrocarbon emissions associated with petroleum production and use. The ethane-based fossil-fuel emission history is strikingly different from bottom-up estimates of methane emissions from fossil-fuel use, and implies that the fossil-fuel source of methane started to decline in the 1980s and probably caused the late twentieth century slow-down in the growth rate of atmospheric methane.

- Highly stable surface modifications of poly(3-caprolactone) (PCL) films by molecular self-assembly to promote cells adhesion and proliferation
  Wang, Z.; Wang, H.; Zheng, W.; Zhang, J.; Zhao, Q.; Wang, S.; Yang, Z.; Kong, D. *Chem. Commun.* **2011**, *47*, 8901-8903.
  Abstract:



A molecular hydrogelator has been used for surface modification of poly(3-caprolactone) (PCL) films to promote cells adhesion and proliferation.

- A generalized supramolecular strategy for self-sorted assembly between donor and acceptor gelators
  Das, A.; Ghosh, S. *Chem. Commun.* **2011**, *47*, 8922-8924.
  Abstract:



Self-sorting among bis-amide functionalized acceptor (NDI) and donor (DAN) gelators is achieved by asymmetric and symmetric placement of the amide groups in the respective chromophores.