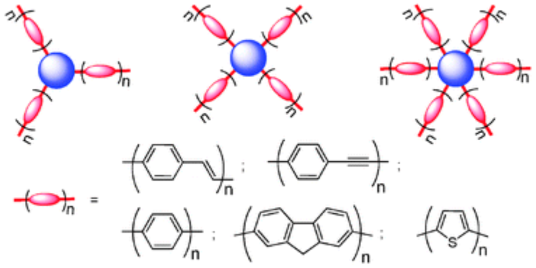
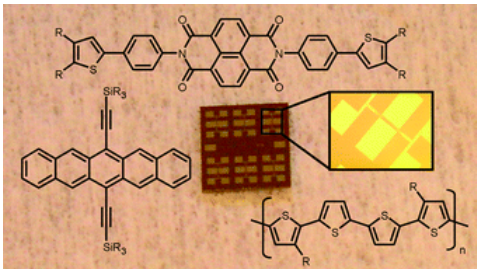
- Star-shaped π-conjugated oligomers and their applications in organic electronics and photonics
  Kanibolotsky, A. L.; Perepichka, I. F.; Skabara, P. J. *Chem. Soc. Rev.* **2010**, *39*, 2695 – 2728.
  Abstract:



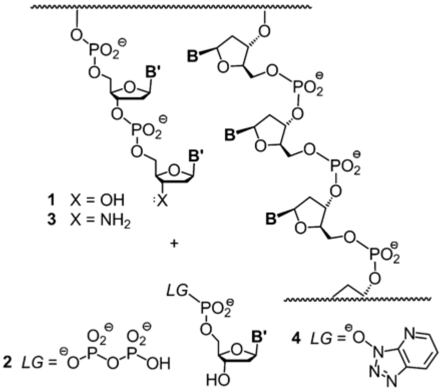
Strategies for the design and construction of non-linear, 2D and 3D conjugated macromolecules are presented in this *critical review*. The materials, termed here as *star-shaped* structures, feature a core unit which may or may not provide conjugated links between arms that radiate like spokes from a central axle. The arms of the macromolecules consist of linear oligomers or irregular conjugated chains lacking a formal repeat unit. The cores range from simple atoms to single or fused aromatic units and can provide a high level of symmetry to the overall structure. The physical properties of the star-shaped materials can be markedly different to their simple, linear conjugated analogues. These differences are highlighted and we report on anomalies in absorption/emission characteristics, electronic energy levels, thermal properties and morphology of thin films. We provide numerous examples for the application of star-shaped conjugated macromolecules in organic semiconductor devices; a comparison of their device performance with those comprising analogous linear systems provides clear evidence that the star-shaped compounds are an important class of material in organic electronics. Moreover, these structures are monodisperse, well-defined, discrete molecules with 100% synthetic reproducibility, and possess high purity and excellent solubility in common organic solvents. They feature many of the attributes of plastic materials (good film-forming properties, thermal stability, flexibility) and are therefore extremely attractive alternatives to conjugated polymers (210 references).

- Electroactive materials for organic electronics: preparation strategies, structural aspects and characterization techniques
  Pron, A.; Gawrys, P.; Zagorska, M.; Djurado, D.; Demadrille, R. *Chem. Soc. Rev.* **2010**, *39*, 2577 – 2632.
  Abstract:



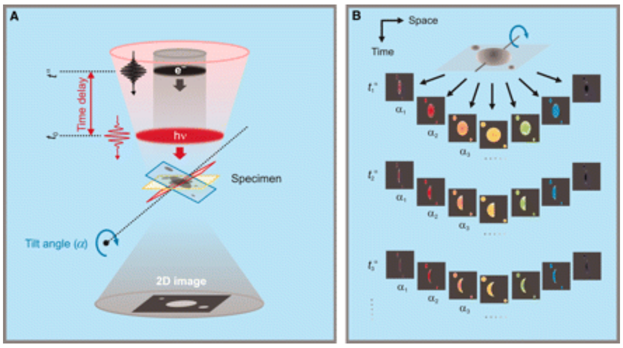
This *critical review* discusses specific chemical and physicochemical requirements which must be met for organic compounds to be considered as promising materials for applications in organic electronics. Although emphasis is put on molecules and macromolecules suitable for fabrication of field effect transistors (FETs), a large fraction of the discussed compounds can also be applied in other organic or hybrid (organic–inorganic) electronic devices such as photodiodes, light emitting diodes, photovoltaic cells, *etc.* It should be of interest to chemists, physicists, material scientists and electrical engineers working in the domain of organic electronics (423 references).

- Templating efficiency of naked DANN
  Kervioa, E.; Hochgesandb, A.; Steinerc, U. E.; Richert, C. *Proc. Nat. Acad. Sci.* **2010**, *107*, 12074-12079.
  Abstract:



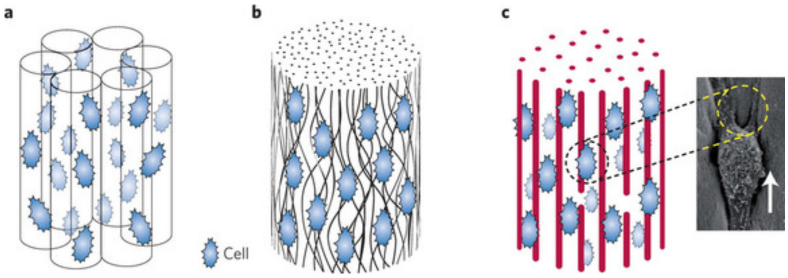
Template-directed synthesis of complementary strands is pivotal for life. Nature employs polymerases for this reaction, leaving the ability of DNA *itself* to direct the incorporation of individual nucleotides at the end of a growing primer difficult to assess. Using 64 sequences, we now find that any of the four nucleobases, in combination with any neighboring residue, support enzyme-free primer extension when primer and mononucleotide are sufficiently reactive, with ≥93% primer extension for all sequences. Between the 64 possible base triplets, the rate of extension for the poorest template, C**A**G, with **A** as templating base, and the most efficient template, T**C**T, with **C** as templating base, differs by less than two orders of magnitude. Further, primer extension with a balanced mixture of monomers shows ≥72% of the correct extension product in all cases, and ≥90% incorporation of the correct base for 46 out of 64 triplets in the presence of a downstream-binding strand. A mechanism is proposed with a binding equilibrium for the monomer, deprotonation of the primer, and two chemical steps, the first of which is most strongly modulated by the sequence. Overall, rates show a surprisingly smooth reactivity landscape, with similar incorporation on strongly and weakly templating sequences. These results help to clarify the substrate contribution to copying, as found in polymerase-catalyzed replication, and show an important feature of DNA as genetic material.

- 4D Electron Tomography
  Kwon, O.-H.; Zewail, A. H. *Science* **2010**, *328*, 1668 – 1673.
  Abstract:



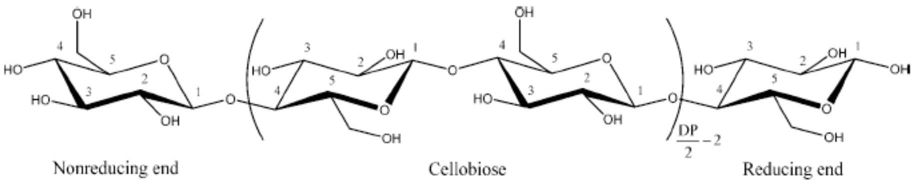
Electron tomography provides three-dimensional (3D) imaging of noncrystalline and crystalline equilibrium structures, as well as elemental volume composition, of materials and biological specimens, including those of viruses and cells. We report the development of 4D electron tomography by integrating the fourth dimension (time resolution) with the 3D spatial resolution obtained from a complete tilt series of 2D projections of an object. The different time frames of tomograms constitute a movie of the object in motion, thus enabling studies of nonequilibrium structures and transient processes. The method was demonstrated using carbon nanotubes of a bracelet-like ring structure for which 4D tomograms display different modes of motion, such as breathing and wiggling, with resonance frequencies up to 30 megahertz. Applications can now make use of the full space-time range with the nanometer-femtosecond resolution of ultrafast electron tomography.

- Regenerative medicine: Noodle gels for cells
  Deming, T. J. *Nature Materials* **2010**, *9*, 535-536.
  Abstract:



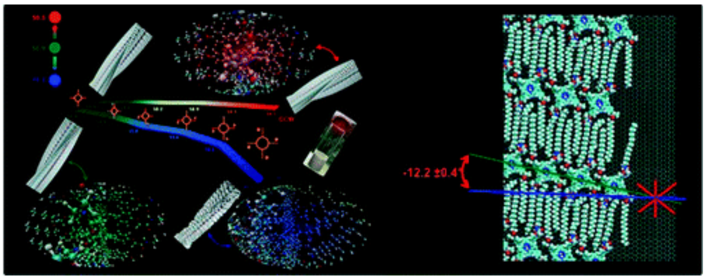
Heating and cooling of peptide amphiphile suspensions converts disorganized nanofibres into liquid-crystalline nanofibre bundles that gel on addition of salts. The noodle-shaped strings of gel can entrap and align cells.

- Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications
  Habibi, Y.; Lucia, L. A.; Rojas, O. J. *Chem. Rev.* **2010,** *110,* 3479–3500.
  Abstract:



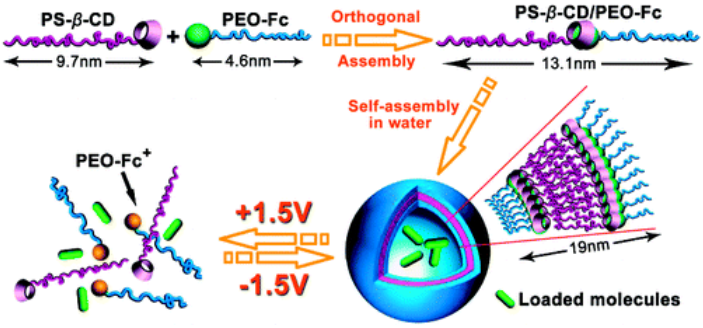
Cellulose constitutes the most abundant renewable polymer resource available today. As a chemical raw material, it is generally well-known that it has been used in the form of fibers or derivatives for nearly 150 years for a wide spectrum of products and materials in daily life. What has not been known until relatively recently is that when cellulose fibers are subjected to acid hydrolysis, the fibers yield defect-free, rod-like crystalline residues.

- Tuning the Supramolecular Chirality of One- and Two-Dimensional Aggregates with the Number of Stereogenic Centers in the Component Porphyrins
  Iavicoli, P.; Xu, H.; Feldborg, L. N.; Linares, M.; Paradinas, M.; Stafstrum, S.; Ocal, C.; Nieto-Ortega, B.; Casado, J.; López Navarrete, J. T.; Lazzaroni, R.; Feyter, S. D.; Amabilino, D. B. *J. Am. Chem. Soc.* **2010**, *132*, 9350–9362.
  Abstract:



A synthetic strategy was developed for the preparation of porphyrins containing between one and four stereogenic centers, such that their molecular weights vary only as a result of methyl groups which give the chiral forms. The low-dimensional nanoscale aggregates of these compounds reveal the profound effects of this varying molecular chirality on their supramolecular structure and optical activity. The number of stereogenic centers influences significantly the self-assembly and chiral structure of the aggregates of porphyrin molecules described here. A scanning tunneling microscopy study of monolayers on graphite shows that the degree of structural chirality with respect to the surface increases almost linearly with the number of stereogenic centers, and only one handedness is formed in the monolayers, whereas the achiral compound forms a mixture of mirror-image domains at the surface. In solution, four hydrogen bonds induce the formation of an H-aggregate, and circular dichroism measurements and theoretical studies indicate that the compounds self-assemble into helical structures. Both the chirality and stability of the aggregates depend critically on the number of stereocenters. The chiral porphyrin derivatives gelate methylcyclohexane at concentrations dependent on the number and position of chiral groups at the periphery of the aromatic core, reflecting the different aggregation forces of the molecules in solution. Increasing the number of stereogenic centers requires more material to immobilize the solvent, in all likelihood because of the greater solubility of the porphyrins. The vibrational circular dichroism spectra of the gels show that all compounds have a chiral environment around the amide bonds, confirming the helical model proposed by calculations. The morphologies of the xerogels (studied by scanning electron microscopy and scanning force microscopy) are similar, although more fibrous features are present in the molecules with fewer stereogenic centers. Importantly, the presence of only one stereogenic center, bearing a methyl group as the desymmetrizing ligand, in a molecule of considerable molecular weight is enough to induce single-handed chirality in both the one- and two-dimensional supramolecular self-assembled structures.

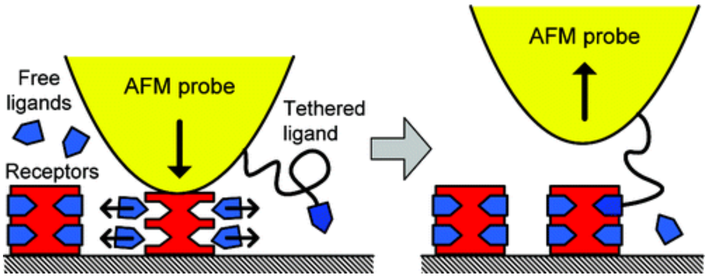
- Voltage-Responsive Vesicles Based on Orthogonal Assembly of Two Homopolymers
  Yan, Q.; Yuan, J.; Cai, Z.; Xin, Y.; Kang, Y.; Yin, Y. *J. Am. Chem. Soc.* **2010**, *132*, 9268–9270.
  Abstract:



Two end-decorated homopolymers, poly(styrene)-β-cyclodextrin (PS-β-CD) and poly(ethylene oxide)-ferrocene (PEO-Fc), can orthogonally self-assemble into a supramolecular diblock copolymer (PS-β-

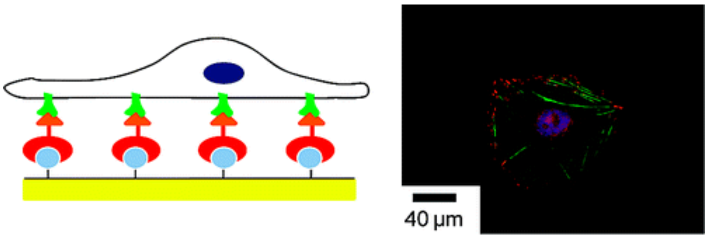
CD/PEO-Fc) in aqueous solutions based on the terminal host–guest interactions. These assemblies can further form supramolecular vesicles, and their assembly and disassembly behaviors can be reversibly switched by voltage through the reversible association and disassociation of the middle supramolecular connection. The vesicles possess an unprecedented property that their assembly or disassembly speed can be controlled by the applied voltage strength. Luminescence spectroscopy demonstrates that the vesicles act as nanocapsules carrying molecules within their hollow cavities and that the external voltage strength accurately regulates the drug release time.

- Mechanical Distortion of Protein Receptor Decreases the Lifetime of a Receptor–Ligand Bond
  Guo, S.; Li, N.; Lad, N.; Ray, C.; Akhremitchev, B. B. *J. Am. Chem. Soc.* **2010**, *132*, 9681–9687.
  Abstract:



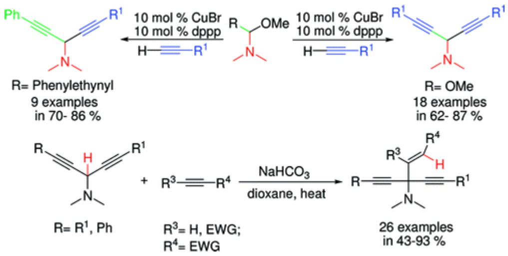
Substantial experimental evidence indicates that the mechanical force applied to pull apart non-covalent molecular bonds (such as receptor–ligand pairs) can significantly decrease the bond lifetime. This evidence is often generated in single-molecule experiments that are designed to specifically test effects of pulling forces. However, the effect of compressive forces on the lifetime of receptor–ligand bonds remains largely unexplored. Here we extend the common usage of the atomic force microscopy technique to study whether compressive forces applied to bound streptavidin–biotin species can significantly accelerate the rate of dissociation. Presented experimental data indicate that compressive forces can substantially decrease the lifetime of the molecular bond. Surprisingly, the efficiency of accelerating dissociation by compressive forces sometimes exceeds the enhancement of the dissociation rate measured in pulling experiments, indicating that compressive forces applied to the bound species might be efficiently used to control the lifetime of adhesion bonds.

- Cell Adhesion to Unnatural Ligands Mediated by a Bifunctional Protein
  Sánchez-Cortés, J.; Bähr, K.; Mrksich, M. *J. Am. Chem. Soc.* **2010**, *132*, 9733–9737.
  Abstract:



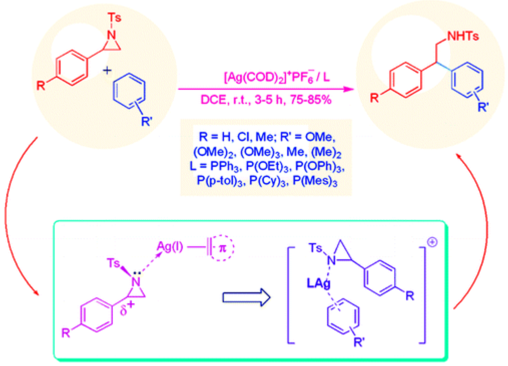
This paper describes a molecular strategy to restore adhesion of cells to surfaces that otherwise do not present ligands that can mediate adhesion. The approach is based on a carbonic anhydrase fusion protein that binds benzenesulfonamides and that also includes the RGD peptide motif that can bind to cell-surface integrin adhesion receptors. In this way, the fusion protein can bind to a monolayer that presents the benzenesulfonamide ligand, thereby positioning the RGD peptide at the surface, where it can mediate the adhesion and spreading of cells. This strategy may provide a general method for promoting the adhesion of cells to non-natural surfaces or to defective biological matrices.

- Copper-Catalyzed Coupling Reaction of C–OMe Bonds Adjacent to a Nitrogen Atom with Terminal Alkynes
  Yao, B.; Zhang, Y.; Li, Y. *J. Org. Chem.* **2010**, *75*, 4554–4561.
  Abstract:



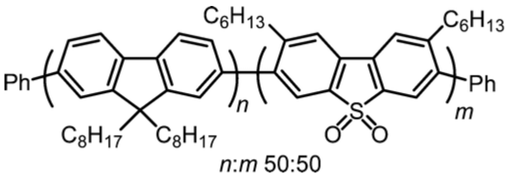
The cross coupling of the C–OMe bond adjacent to a nitrogen atom in dialkoxy-*N*,*N*-dialkylmethanamines with terminal alkynes was efficiently approached in the presence of copper catalyst under mild conditions to give 3-amino-1,4-diynes in good yields. The reaction is promoted by phosphine ligands and the chemistry provides a simple and efficient route to 3-amino-1,4-diynes. Importantly, the Michael addition occurred with as-prepared 3-amino-1,4-diynes to give the useful Michael-adducts containing *tert*-alkylamines in a very convenient way. Further studies revealed that (*E*)-1,5-diarylpent-1-en-4-yn-3-one was formed through the rearrangement by using the neutral alumina column, and the corresponding imine 2-(1,5-diphenylpent-2-en-4-ynylideneamino)ethanol was obtained in the presence of AgOTf.

- Silver(I)–Diene Complexes as Versatile Catalysts for the *C*-Arylation of *N*-Tosylaziridines: Mechanistic Insight from In Situ Diagnostics
  Bera, M.; Roy, S. *J. Org. Chem.* **2010**, *75*, 4402–4412.
  Abstract:



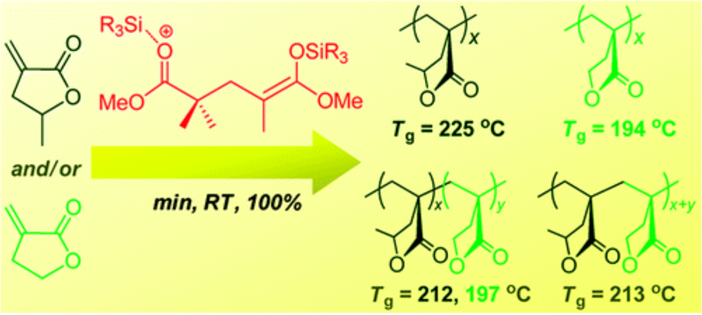
Silver(I) complex $[Ag(diene)_2]^+Y^-$ (where diene = cyclooctadiene, norbornadiene, and 1,3-cyclohexadiene; $Y^- = PF_6^-$, BF_4^-) efficiently catalyzes the arylation of *N*-tosylaziridines with arenes and heteroarenes under ambient condition to provide the corresponding β-aryl amine derivatives with excellent regioselectivity. To understand the nature of substrate activation, and initial bond breaking/making steps, the following studies were conducted with the help of in situ NMR (^1H, ^{31}P, ^{109}Ag) and ESI-MS probe: (I) evaluation of Hammett reaction constant (ρ); (II) correlation of initial rate (*k*) versus cone angle (θ) of ligand L for reactions mediated by $[Ag(COD)_2]PF_6/L$ (where L is a phosphine or a phosphite ligand); (III) identification of silver–arene intermediates in solution; and (IV) correlation of initial rate (*k*) with $\Delta_{HOMO-LUMO}$ of $[Ag(diene)_2]PF_6$ obtained from preliminary DFT studies. Study I led to a ρ-value of −0.586, indicating that the extent of electrophilic perturbation is considerably less than a typical Lewis acid catalyzed process. Study II indicated that initial rate (*k*) increases with concomitant increase in θ, as well with $\Delta^{31}P_{(\text{complex–ligand})}$, which corroborates to a mechanism involving prior ligand dissociation. Study III showed the plausible formation of $[\text{Ag(diene)(arene)}]^+$ and $[\text{Ag(arene)}_2]^+$ as reactive species in solution. Study IV showed that the dependence of initial rate (*k*) with diene ligand is in the order COD > NBD > CHD; which corresponds well with the order of hardness of the respective Ag(I) complexes.

- Synthesis and Spectroscopy of Poly(9,9-dioctylfluorene-2,7-diyl-*co*-2,8-dihexyldibenzothiophene-*S,S*-dioxide-3,7-diyl)s: Solution-Processable, Deep-Blue Emitters with a High Triplet Energy
  Kamtekar, K. T.; Vaughan, H. L.; Lyons, B. P.; Monkman, A. P.; Pandya, S. U.; Bryce, M. R. *Macromolecules* **2010**, *43*, 4481–4488.
  Abstract:



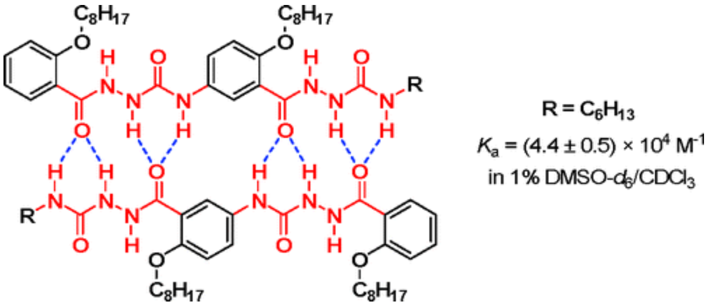
Poly(9,9-dioctylfluorene-2,7-diyl-*co*-2,8-dihexyldibenzothiophene-*S,S*-dioxide-3,7-diyl) copolymers (pF-S_6 **8**–**10**) of varying composition have been synthesized by Suzuki−Miyaura polymerization. The hexyl substituents on the dibenzothiophene-*S,S*-dioxide (S) units improve the solubility of the copolymers and increase the dihedral angles in the backbone; this shifts the emission deep into the blue (λ_{max} 420 nm for films of **10**) and increases the photoluminescence quantum yield compared with previous pF-S copolymers containing non-alkylated S units. The backbone twist restricts formation of the intramolecular charge transfer (ICT) state for low incorporation ratios of S_6 units. The triplet energy of these new copolymers increases as the percentage of the S_6 unit increases (i.e., 15, 30, 50%: **8** → **9** → **10**). The alternating copolymer **10** has a sufficiently high triplet energy (E_T 2.46 eV for onset of phosphorescence) to host a green phosphorescent iridium guest emitter, as demonstrated in electroluminescence studies which showed emission exclusively from the guest complex.

- Living Polymerization of Naturally Renewable Butyrolactone-Based Vinylidene Monomers by Ambiphilic Silicon Propagators
  Miyake, G. M.; Zhang, Y.; Chen, E. Y.-X. *Macromolecules* **2010**, *43*, 4902–4908.
  Abstract:



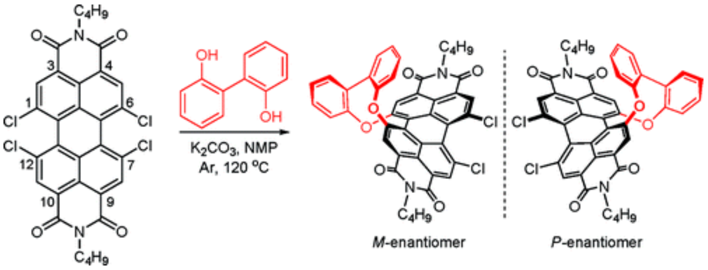
Naturally renewable butyrolactone-based vinylidene monomers, α-methylene-γ-butyrolactone (MBL) and γ-methyl-α-methylene-γ-butyrolactone (MMBL), have been successfully polymerized in a rapid and living fashion, using ambiphilic silicon propagating species consisting of both the nucleophilic silyl ketene acetal (SKA) initiating moiety and the electrophilic silylium catalyst. Uniquely, the R_3Si^+ catalyst is derived directly from the SKA initiator upon *in situ* oxidative activation with a catalytic amount of the trityl borate activator. Investigations into effects of SKA (thus the resulting R_3Si^+ catalyst) and activator (thus the resulting counteranion) structures have revealed that the $Me_2C{=}C(OMe)OSi^iBu_3/Ph_3CB(C_6F_5)_4$ combination is the most active *and* controlled system for (M)MBL polymerizations. Thus, under ambient conditions and with a low catalyst loading (0.05 mol % relative to monomer), this polymerization system rapidly (within 10 min) and completely converts MMBL to PMMBL with controlled low to high (M_n = 5.43 × 10^5 kg/mol) MW's and narrow MW distributions (1.01−1.06). Well-defined block copolymers of MBL and MMBL with MMA as well as block and statistical copolymers of MBL with MMBL have also been readily synthesized. Atactic homopolymers, PMBL and PMMBL, produced herein exhibit high glass transition temperatures (T_g's) of 194 and 225 °C, respectively, representing T_g enhancements of 90 °C (for PMBL) and 120 °C (for PMMBL) over the T_g of the typical atactic PMMA. The critical MW of PMMBL has been estimated to be 47 kg/mol.

- Multiple Hydrogen-Bond-Mediated Molecular Duplexes Based on the Self-Complementary Amidourea Motif
  Chu, W. J.; Yang, Y.; Chen, C.-F. *Org. Lett.* **2010**, *12*, 3156–3159.
  Abstract:



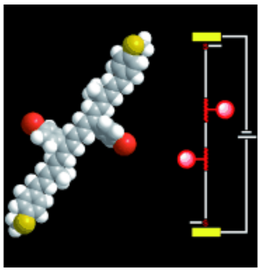
The self-complementary amidourea motif, which was stabilized by four intermolecular tricenter hydrogen bonds, was investigated in solution and in the solid state. Extensive studies on oligomer 2 indicated that the hydrogen-bonding mode could persist in longer molecular duplexes based on the amidourea motif. The dimerization constants of 2b·2b in various DMSO-d_6/$CDCl_3$ mixtures were determined quantitatively by ^{1}H NMR dilution studies, which suggested that the homoduplex was highly stable in low polar solventsDue to their strength, directionality, specificity, cooperativity, and reversibility, multipoint hydrogen-bonding motifs are the cornerstones of the biological recognition and assembly processes and increasingly feature in the design of functional organic materials and supramolecular polymers.

- Perylene Bisimides with Rigid 2,2′-Biphenol Bridges at Bay Area as Conjugated Chiral Platforms
  Xie, Z.; Würthner, F. *Org. Lett.* **2010**, *12*, 3204–3207.
  Abstract:



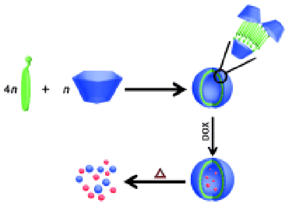
Facile nucleophilic substitution of two chlorine atoms by 2,2′-biphenol at one of the two bay areas (1,12- and 6,7-positions) of core-tetrachlorinated perylene bisimide afforded a novel, completely desymmetrized perylene bisimide building block, which could be further functionalized by substitution of the remaining two chlorine atoms. The atropisomers (*P*- and *M*-enantiomers) of the core twisted perylene bisimides were resolved by HPLC on a chiral column at room temperature, and the activation parameters for racemization were elucidated.

- Conductance Control in Stabilized Carotenoid Wires
  Maeng, J.; Kim, S. B.; Lee, N. J.; Choi, E.; Jung, S.-Y.; Hong, I.; Bae, S.-H.; Oh, J. T.; Lim, B.; Kim, J. W.; Kang, C. J.; Koo, S. *Chem. Eur. J.* **2010**, *16*, 7395-7399.
  Abstract:



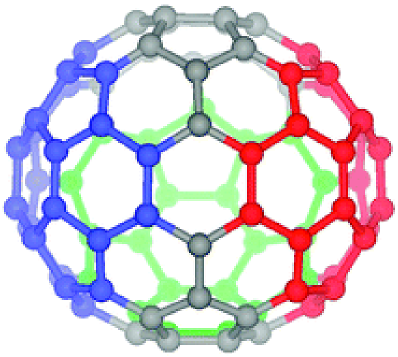
Tunable carots: Construction of the stable carotenoid wires with a specific conductance value is possible by the attachment of phenyl groups to the polyene chain to overcome the in vitro instability of natural carotenoids, the perfect molecular wires utilized in various biological processes. Diverse electronic natures of the substituents on the phenyl groups provide the carotenoids with tunable conductance (see figure).

- Temperature-Controlled Supramolecular Vesicles Modulated by *p*-Sulfonatocalix[5]arene with Pyrene
  Wang, K.; Guo, D.-S.; Liu, Y. *Chem. Eur. J.* **2010**, *16*, 8006-8011.
  Abstract:



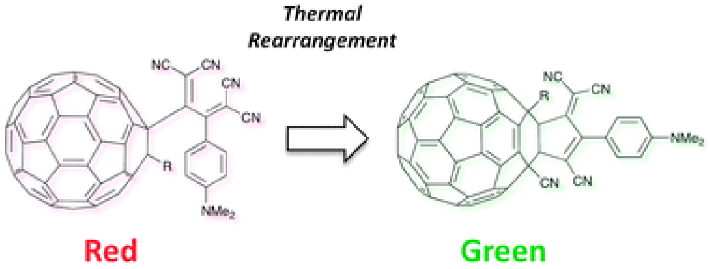
Supramolecular vesicles were successfully constructed on the basis of host-guest complex formation between *p*-sulfonatocalix[5]arene and 1-pyrenemethylaminium. The obtained vesicles exhibit benign water solubility, self-labeled fluorescence, and more importantly, temperature-response characteristics; these features mean that the vesicles can act as potential delivery models for special substrates (see figure; DOX=doxorubicin hydrochloride).

- Structural similarities in $C_s(16)$-C_{86} and $C_2(17)$-C_{86}
  Wang, Z.; Yang, H.; Jiang, A.; Liu, Z.; Olmstead, M. M.; Balch, A. L. *Chem. Commun.* **2010**, *46*, 5262 – 5264.
  Abstract:



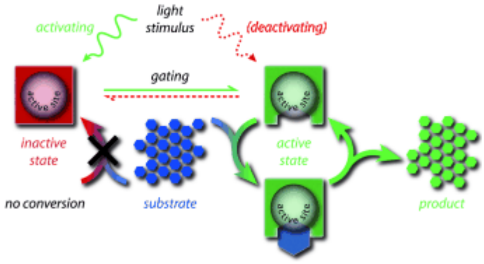
We report an analysis of the similar structures of $C_s(16)$-C_{86} and $C_2(17)$-C_{86} from a single crystal X-ray diffraction study of $Cs(16)/C_2(17)$-C_{86}·(nickel octaethylporphyrin)·2toluene.

- Unprecedented thermal rearrangement of push–pull-chromophore–[60]fullerene conjugates: formation of chiral 1,2,9,12-tetrakis-adducts
  Yamada, M.; Schweizer, W. B.; Schoenebeck, F.; Diederich, F. *Chem. Commun.* **2010**, *46*, 5334 – 5336.
  Abstract:



Push–pull-chromophore–[60]fullerene conjugates featuring N,N-dimethylanilino-substituted 1,1,4,4-buta-1,3-dienes directly attached to the carbon sphere are transformed into chiral 1,2,9,12-tetrakis-adducts by a novel thermal rearrangement pathway.

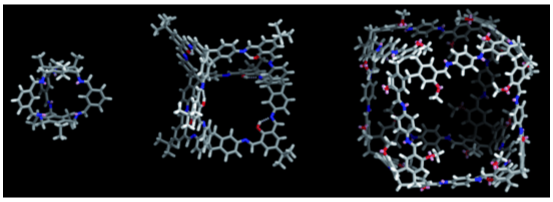
- Artificial Light-Gated Catalyst Systems
  Stoll, R. S.; Hecht, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 5054 –5075.
  Abstract:



Having control over an entity or even an entire process is arguably the ultimate demonstration of its understanding and it will enable its potential to be fully exploited. With this in mind, chemists have not only been creating and optimizing a myriad of different catalysts for most (relevant) chemical reactions over the past decades, but have recently started to implement controlling elements into

the catalyst design. These incorporated gates operate upon exposure to suitable control stimuli, and light represents perhaps the scientifically and technologically most attractive stimulus. In principle, irradiation can thereby induce activity and selectivity in a given catalyst system with high spatial and temporal control, leading to an overall localization and amplification of an optical signal and translation into chemical action. While nature has developed and utilized this concept, in particular in the processes of vision and photomovement, such artificial photocontrolled catalyst systems offer unique opportunities and have high potential for future applications. In this Review, we outline the general concept of light-gated catalysis based on photocaged and also photoswitchable systems, and discuss relevant examples of the past and recent literature.

- Shape-Persistent Organic Cage Compounds by Dynamic Covalent Bond Formation
  Mastalerz, M. *Angew. Chem. Int. Ed*. **2010**, *49*, 5042–5053.
  <u>Abstract:</u>



One area of supramolecular chemistry involves the synthesis of discrete three-dimensional molecules or supramolecular aggregates through the coordination of metals. This field also concerns the chemistry of supramolecular cage compounds constructed through the use of such coordination bonds. To date, there exists a broad variety of supramolecular cage compounds; however, analogous organic cage compounds formed with only covalent bonds are relatively rare. Recent progress in this field can be attributed to important advances, not least the application of dynamic covalent chemistry. This concept makes it possible to start from readily available precursors, and in general allows the synthesis of cage compounds in fewer steps and usually higher yields.