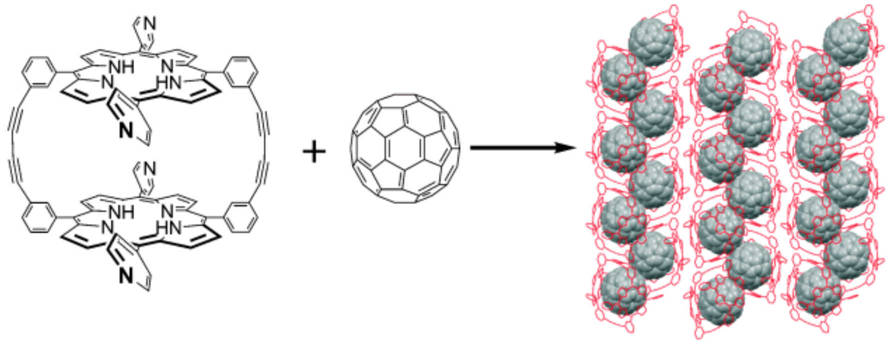
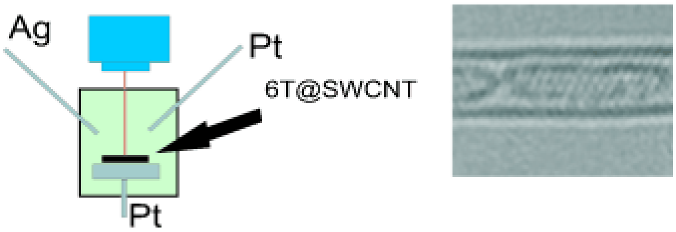
- Supramolecular Structures and Photoelectronic Properties of the Inclusion Complex of a Cyclic Free-Base Porphyrin Dimer and C_{60}
  Nobukuni, H.; Shimazaki, Y.; Uno, H.; Naruta, Y.; Ohkubo, K.; Kojima, T.; Fukuzumi, S.; Seki, S.; Sakai, H.; Hasobe, T.; Tani, F. *Chem.-Eur. J.* **2010**, *16*, 11611-11623.
  Abstract:



A cyclic free-base porphyrin dimer $H_4\text{-CPD}_{Py}$ (CPD=cyclic porphyrin dimer) linked by butadiyne moieties bearing 4-pyridyl groups self-assembles to form a novel porphyrin nanotube in the crystalline state. The cyclic molecules link together through nonclassical C—H⋅⋅⋅N hydrogen bonds and π–π interactions of the pyridyl groups along the crystallographic *a* axis. $H_4\text{-CPD}_{Py}$ includes a C_{60} molecule in its cavity in solution. In the crystal structure of the inclusion complex ($C_{60}\subset H_4\text{-CPD}_{Py}$), the dimer "bites" a C_{60} molecule by tilting the porphyrin rings with respect to each other, and there are strong π–π interactions between the porphyrin rings and C_{60}. The included C_{60} molecules form a zigzag chain along the crystallographic *b* axis through van der Waals contacts with each other. Femtosecond laser flash photolysis of $C_{60}\subset H_4\text{-CPD}_{Py}$ in the solid state with photoexcitation at 420 nm shows the formation of a completely charge-separated state $\{H_4\text{-CPD}_{Py}^{\cdot+}+C_{60}^{\cdot-}\}$, which decays with a lifetime of 470 ps to the ground state. The charge-carrier mobility of the single crystal of $C_{60}\subset H_4\text{-CPD}_{Py}$ was determined by flash photolysis time-resolved microwave conductivity (FP-TRMC) measurements. $C_{60}\subset H_4\text{-CPD}_{Py}$ has an anisotropic charge mobility ($\Sigma\mu=0.16$ and $0.13\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$) along the zigzag chain of C_{60} (which runs at 45° and parallel to the crystallographic *b* axis). To construct a photoelectrochemical cell, $C_{60}\subset H_4\text{-CPD}_{Py}$ was deposited onto nanostructured SnO_2 films on a transparent electrode. The solar cell exhibited photovoltaic activity with an incident photon to current conversion efficiency of 17 %.

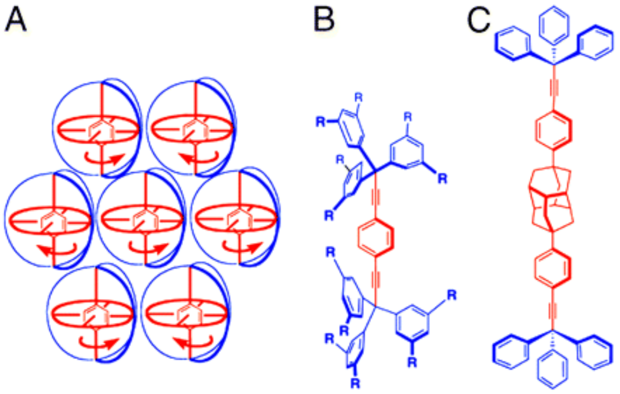
- Sexithiophene Encapsulated in a Single-Walled Carbon Nanotube: An In Situ Raman Spectroelectrochemical Study of a Peapod Structure
  Kalb, M. ; Kavan, L.; Gorantla, S.; Gemming, T.; Dunsch, L. *Chem.-Eur. J.* **2010**, *16*, 11753-11759.
  Abstract:



The interaction of single-walled carbon nanotubes (SWCNTs) and *α*-sexithiophene (6T) was studied by Raman spectroscopy and by in situ Raman spectroelectrochemistry. The encapsulation of 6T in SWCNT and its interaction causes a bleaching of its photoluminescence, and also small shifts of its

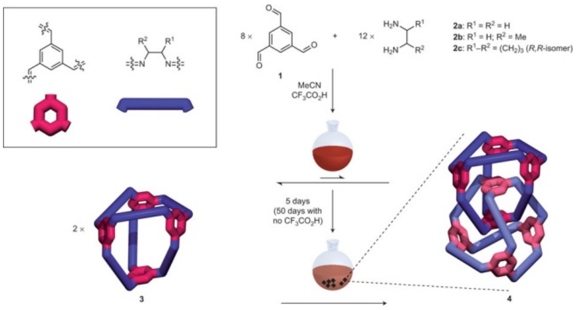
Raman bands. The Raman features of the SWCNT with embedded 6T (6T-peapods) change in both intensity and frequency compared to those of pristine SWCNT, which is a consequence of a change of the resonant condition. Electrochemical doping demonstrated that the electrode potential applied to the SWCNT wall causes changes in the embedded 6T. The effects of electrochemical charging on the Raman features of pristine SWCNT and 6T@SWCNT were compared. It is shown that the interaction of SWCNT with 6T also changes the electronic structure of SWCNT in its charged state. This change of electronic structure is demonstrated both for semiconducting and metallic tubes.

- Symmetry and dynamics of molecular rotors in amphidynamic molecular crystals
  Karlen, S. D.; Reyes, H.; Taylor, R. E.; Khan, S. I.; Hawthorne, M. F.; Garcia-Garibay, M. A. *Proc. Nat. Acad. Sci. USA* **2010**, *107*, 14973-14977.
  Abstract:



Rotary biomolecular machines rely on highly symmetric supramolecular structures with rotating units that operate within a densely packed frame of reference, stator, embedded within relatively rigid membranes. The most notable examples are the enzyme FoF1 ATP synthase and the bacterial flagellum, which undergo rotation in steps determined by the symmetries of their rotators and rotating units. Speculating that a precise control of rotational dynamics in rigid environments will be essential for the development of artificial molecular machines, we analyzed the relation between rotational symmetry order and equilibrium rotational dynamics in a set of crystalline molecular gyroscopes with rotators having axial symmetry that ranges from two- to fivefold. The site exchange frequency for these molecules in their closely related crystals at ambient temperature varies by several orders of magnitude, up to *ca.* 4.46 × 10^8 s^{-1}.

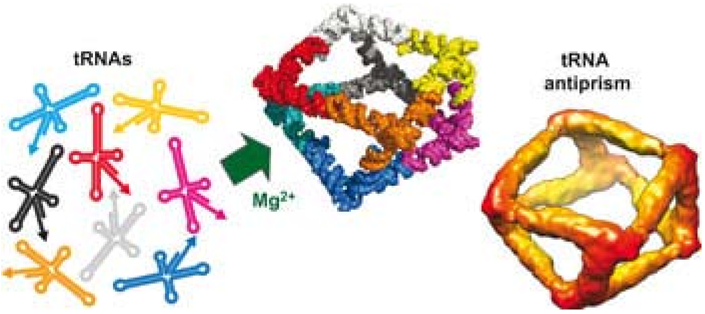
- Interlocked molecules: Linking rings without templates
  Beves, J. E.; Leigh, D. A. *Nature Chemistry* **2010**, *2*, 708 – 710.
  Abstract:



In 1983, Jean-Pierre Sauvage hit on the idea of using a metal ion as a template to gather and organize ligands into a spatial arrangement that could be used to direct the formation of catenanes —

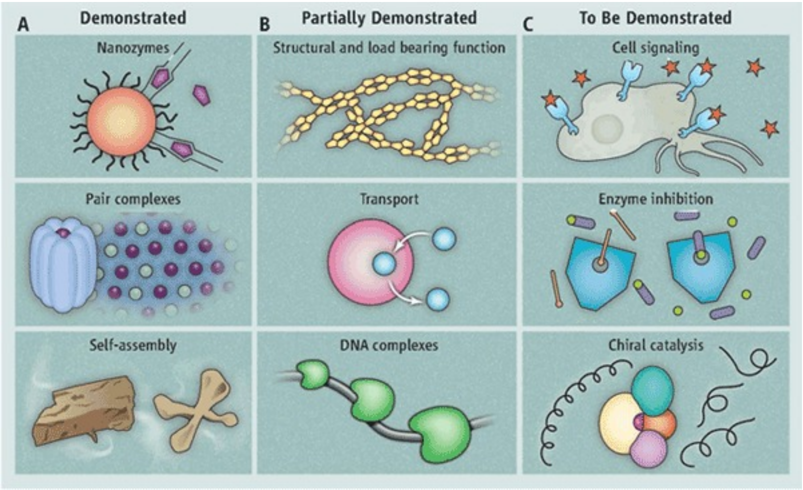
mechanically interlocked rings that cannot be separated from each other without breaking at least one chemical bond. The results were dramatic and their influence far-reaching; the efficiency of the interlocking template reactions were often an order of magnitude better than those of typical 'statistical' or 'covalently directed' reactions, and their simplicity shortened the synthetic routes to just four or five steps from around ten to twenty.

- A polyhedron made of tRNAs
  Severcan, I.; Geary, C.; Chworos, A.; Voss, N.; Jacovetty, E.; Jaeger, L. *Nature Chemistry* **2010**, *2*, 772 – 779.
  Abstract:



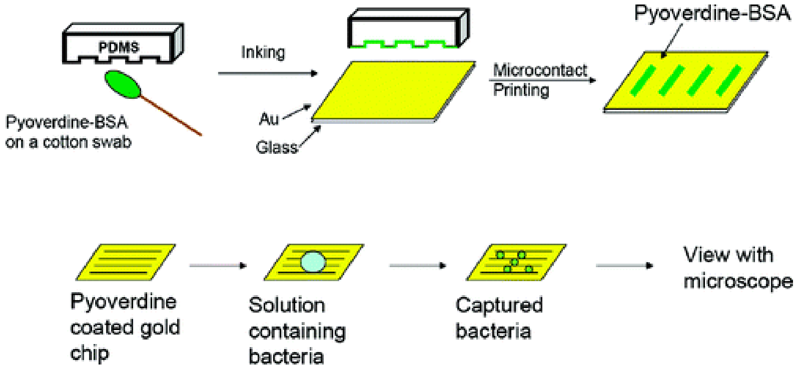
Supramolecular assembly is a powerful strategy used by nature to build nanoscale architectures with predefined sizes and shapes. With synthetic systems, however, numerous challenges remain to be solved before precise control over the synthesis, folding and assembly of rationally designed three-dimensional nano-objects made of RNA can be achieved. Here, using the transfer RNA molecule as a structural building block, we report the design, efficient synthesis and structural characterization of stable, modular three-dimensional particles adopting the polyhedral geometry of a non-uniform square antiprism. The spatial control within the final architecture allows the precise positioning and encapsulation of proteins. This work demonstrates that a remarkable degree of structural control can be achieved with RNA structural motifs for the construction of thermostable three-dimensional nano-architectures that do not rely on helix bundles or tensegrity. RNA three-dimensional particles could potentially be used as carriers or scaffolds in nanomedicine and synthetic biology.

- Inorganic Nanoparticles as Protein Mimics
  Kotov, N. A. *Science* **2010**, *330*, 188 – 189.
  Abstract:



Water-soluble inorganic nanoparticles (NPs) and globular proteins (GPs) might seem "as different as chalk and cheese," especially in the interior. The chemical structure of GPs is usually exact and well-defined, whereas NPs are almost always formed as a mixture of sizes and variation of shapes. The complexity and dynamism of three-dimensional atomic organization inside the protein globules and related functionalities are not present in the impenetrable crystalline cores of NPs. However, NPs and GPs do reveal similarities in overall size, charge, and shape, and the exterior surfaces of NPs can be coated with organic functional groups similar to those exposed by GPs, which suggest that NPs could function as protein mimics. This option is attractive because NPs are usually cheaper and more stable than proteins, but can they actually display the same functionalities and achieve enough specificity to replace proteins?

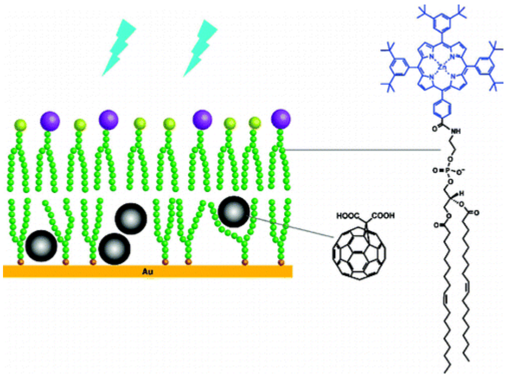
- Selective Capture and Identification of Pathogenic Bacteria Using an Immobilized Siderophore
  Doorneweerd, D. D.; Henne, A. W.; Reifenberger, R. G.; Low, P. S. *Langmuir* **2010**, *26,* 15424–15429.
  Abstract:



Rapid identification of infectious pathogens constitutes an important step toward limiting the spread of contagious diseases. Whereas antibody-based detection strategies are often selected because of their speed, mutation of the pathogen can render such tests obsolete. In an effort to develop a rapid yet mutation-proof method for pathogen identification, we have explored the use of “immutable ligands” to capture the desired microbe on a detection device. In this “proof-of-principle” study, we immobilize pyoverdine, a siderophore that *Pseudomonas aeruginosa* must bind to obtain iron, onto gold-plated glass chips and then examine the siderophore’s ability to capture *P. aeruginosa* for its subsequent identification. We demonstrate that exposure of pyoverdine-coated chips to increasing dilutions of *P. aeruginosa* allows detection of the bacterium down to concentrations as low as 10^2/mL. We further demonstrate that printing of the siderophore in a periodic pattern on the detection chip enables a sensitive method of detecting the bound pathogen by a Fourier transform analysis of light scattered by the patterned chip. Because unrelated bacteria are not captured on the pyoverdine chip, we conclude that pyoverdine can be exploited for the specific binding and identification of *P. aeruginosa.* It follows that the utilization of other microbe-specific “immutable ligands” may allow the specific identification of their cognate pathogens.

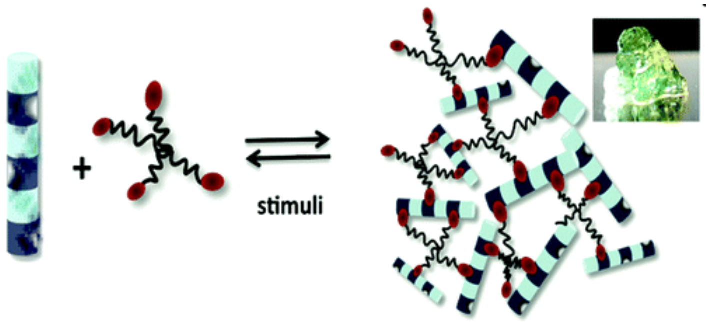
- Photocurrent Generation from Porphyrin/Fullerene Complexes Assembled in a Tethered Lipid Bilayer
  Zhan, W.; Jiang, K.; Smith, M. D.; Bostic, H. E.; Best, M. D.; Auad, M. L.; Ruppel, J. V.; Kim, C. ; Zhang, X. P. *Langmuir* **2010**, *26*, 15671-15679.

Abstract:



A modular photocurrent generation system, based on amphiphilic porphyrin and fullerene species assembled in a tethered lipid bilayer matrix, is reported here. The key findings are (1) the amount of photoactive species can be quantitatively controlled in each leaflet of the bilayer and (2) the sequential formation of the bilayer allows a directional organization of these agents on electrodes. Photocurrent generation from seven differently configured photoactive bilayers is studied, which reveals several critical factors in achieving efficient photoinduced electron transfer across lipid membranes. Detailed fluorescence characterization is performed on porphyrin samples either in liposomes or surface-tethered bilayers; and the observed fluorescence quenching is correlated with photocurrents generated from the electrode-immobilized lipid films. The potential usefulness of this lipid-based approach is discussed in connection to several existing molecular photovoltaic systems.

- Stimuli-Responsive Smart Gels Realized via Modular Protein Design
  Grove, T. Z.; Osuji, C. O.; Forster, J. D.; Dufresne, E. R.; Regan, L. *J. Am. Chem. Soc.* **2010**, *132*, 14024–14026.
  Abstract:

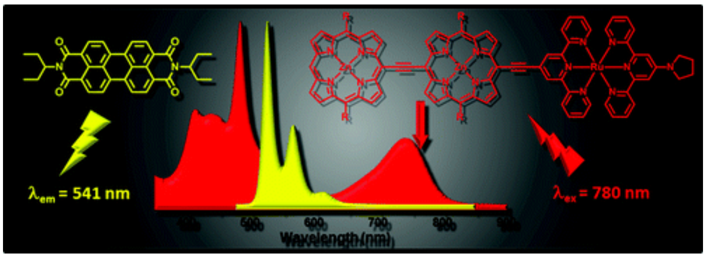


Smart gels have a variety of applications, including tissue engineering and controlled drug delivery. Here we present a modular, bottom-up approach that permits the creation of protein-based smart gels with encoded morphology, functionality, and responsiveness to external stimuli. The properties of these gels are encoded by the proteins from which they are synthesized. In particular, the strength and density of the network of intermolecular cross-links are specified by the interactions of the gels' constituent protein modules with their cognate peptide ligands. Thus, these gels exhibit stimuli-responsive assembly and disassembly, dissolving (or gelling) under conditions that weaken (or strengthen) the protein−peptide interaction. We further demonstrate that such gels can encapsulate and release both proteins and small molecules and that their rheological properties are well suited for biomedical applications.

- Supermolecular-Chromophore-Sensitized Near-Infrared-to-Visible Photon Upconversion

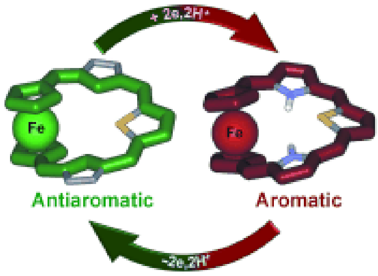
Singh-Rachford, T. N.; Nayak, A.; Muro-Small, M. L.; Goeb, S.; Therien, M. J.; Castellano, F. N. *J. Am. Chem. Soc.* **2010**, *132*, 14203–14211.

Abstract:



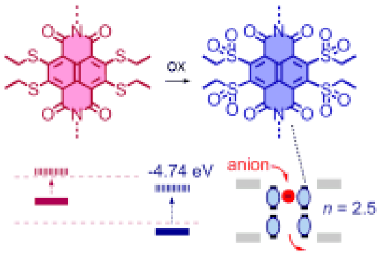
Selective near-IR (NIR) excitation (780 nm) of the conjugated supermolecule ruthenium(II) [15-(4′-ethynyl-(2,2′;6′,2″-terpyridinyl))-bis[(5,5′,-10,20-di(2′,6′-bis(3,3-dimethylbutoxy)phenyl)porphinato) zinc(II)]ethyne][4′-pyrrolidin-1-yl-2,2′;6′,2″-terpyridine] bis(hexafluorophosphate) (Pyr1RuPZn2) in solutions containing N,N-bis(ethylpropyl)perylene-3,4,9,10-tetracarboxylicdiimide (PDI) or tetracene gives rise to a substantial anti-Stokes energy gain (PDI, 0.70 eV; tetracene, 0.86 eV). Experimental data clearly demonstrate that this upconverted fluorescence signal is produced via Pyr1RuPZn2-sensitized triplet−triplet annihilation (TTA) photochemistry. The TTA process was confirmed by the quadratic dependence of the integrated 1PDI* emission centered at 541 nm derived from 780 nm laser excitation. The T1→Tn excited state absorption decay of Pyr1RuPZn2, monitored at 900 nm as a function of PDI concentration, revealed Stern−Volmer and bimolecular quenching constants of 10 048 M−1 and 5.9 × 108 M−1 s−1, respectively, for the PDI triplet sensitization process. The T1→Tn PDI extinction coefficient at 560 nm (εT = 6.6 × 104 M−1 cm−1) was determined through the triplet energy transfer method utilizing anthracene as the donor chromophore. 3PDI* transient triplet absorption dynamics observed as a function of 485 nm incident nanosecond pump laser fluence demonstrate a bimolecular 3PDI*−3PDI* TTA rate constant (kTT = 1.0 ± 0.2 × 109 M−1 s−1). The maximum quantum yield of the supermolecule-sensitized PDI upconverted emission (ΦUC = 0.0075 ± 0.0002) was determined relative to [Os(phen)3][PF6]2 at an incident laser power of 22 mW at 780 nm. This study successfully demonstrates NIR-to-visible photon upconversion and achieves a new record anti-Stokes shift of 0.86 eV for sensitized TTA, using the supermolecular Pyr1RuPZn2sensitizer. The stability of the Pyr1RuPZn2/PDI chromophore combination is readily apparent as continuous irradiation at 780 nm produces 541 nm centered fluorescence with no significant decrease in intensity measured over time domains exceeding several hours. The molecular components of these NIR-to-vis upconverting compositions illustrate that substantial anti-Stokes energy gains via a TTA process can be effortlessly realized.

- π Conjugation Transmitted across a d-Electron Metallocene in Ferrocenothiaporphyrin Macrocycles
  Simkowa, I.; Latos-Grażyński, L.; Stępień, M. *Angew. Chem. Int. Ed.* **2010**, *49,* 7665–7669.
  Abstract:



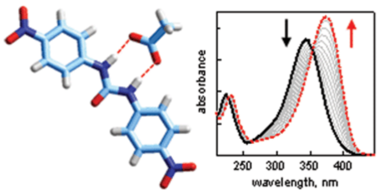
Setting the 'cene: The structural features of ferrocenophanes and porphyrinoids are combined in ferrocene–porphyrin hybrids. Ferrocenothiaporphyrin (see picture, green) and dihydroferrocenothiaporphyrin (red) are macrocyclic antiaromatic and aromatic systems, respectively. These two systems provide evidence for direct transmission of π-electron conjugation across a d-electron metallocene.

- A Chiral and Colorful Redox Switch: Enhanced π Acidity in Action
  Míšek, J.; Jentzsch, A. V.; Sakurai, S.; Emery, D.; Mareda, J.; Matile, S. *Angew. Chem. Int. Ed.* **2010**, *49*, 7680–7683.
  Abstract:



Deep blue diving: π Acidities up to a new record of −4.74 eV are made possible with simple sulfur redox chemistry (see scheme). This attractive method is able to generate exceptional electron affinities and anion transport efficiencies for applications in optoelectronic devices, medicinal chemistry, and anion–π catalysis.

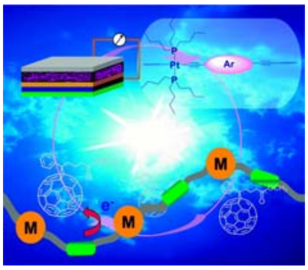
- Anion recognition by hydrogen bonding: urea-based receptors
  Amendola, V.; Fabbrizzi, L.; Mosca, L. *Chem. Soc. Rev.* **2010**, *39*, 3889-3915.
  Abstract:



Since 1992 a variety of urea-based anion receptors have been synthesised, of varying complexity and sophistication. This *critical review* will focus on some distinctive aspects of anion recognition by urea derivatives, with a special reference to: (i) design and synthesis, (ii) methodologies for the investigation of the receptor–anion interaction in solution, (iii) the interpretation of the solution behaviour on the basis of the structural interplay between the receptor and the anion. It will be shown that the efficiency of urea as a receptor subunit depends on the presence of two proximate polarised N–H fragments, capable (i) of chelating a spherical anion or (ii) of donating two parallel H-bonds to the oxygen atoms of a carboxylate or of an inorganic oxoanion, a property which is shared with other diamides, *e.g.* squaramide. The wide use of urea in the design of neutral anion receptors seems to depends on the ease of its synthesis, in particular through the reaction of a primary amine group with an isocyanate, which allows the high-yield preparation of symmetrically and unsymmetrically substituted derivatives (83 references).

- Organometallic Photovoltaics: A New and Versatile Approach for Harvesting Solar Energy Using Conjugated Polymetallaynes
  Wong, W.-Y.; Ho, C.-L. *Acc. Chem. Res.* **2010**, *43*, 1246–1256.

Abstract:

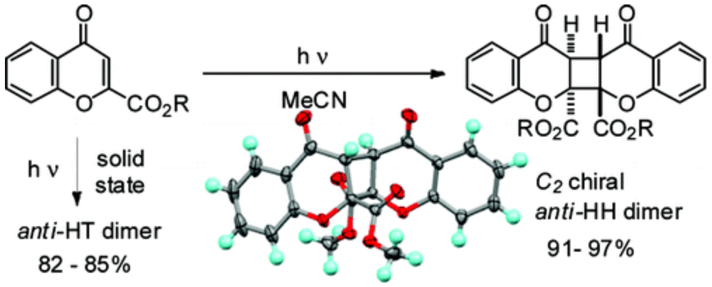


Energy remains one of the world’s great challenges. Growing concerns about limited fossil fuel resources and the accumulation of CO_2 in the atmosphere from burning those fuels have stimulated tremendous academic and industrial interest. Researchers are focusing both on developing inexpensive renewable energy resources and on improving the technologies for energy conversion.

Solar energy has the capacity to meet increasing global energy needs. Harvesting energy directly from sunlight using photovoltaic technology significantly reduces atmospheric emissions, avoiding the detrimental effects of these gases on the environment. Currently inorganic semiconductors dominate the solar cell production market, but these materials require high technology production and expensive materials, making electricity produced in this manner too costly to compete with conventional sources of electricity. Researchers have successfully fabricated efficient organic-based polymer solar cells (PSCs) as a lower cost alternative. Recently, metalated conjugated polymers have shown exceptional promise as donor materials in bulk-heterojunction solar cells and are emerging as viable alternatives to the all-organic congeners currently in use. Among these metalated conjugated polymers, soluble platinum(II)-containing poly(arylene ethynylene)s of variable bandgaps (~1.4–3.0 eV) represent attractive candidates for a cost-effective, lightweight solar-energy conversion platform.

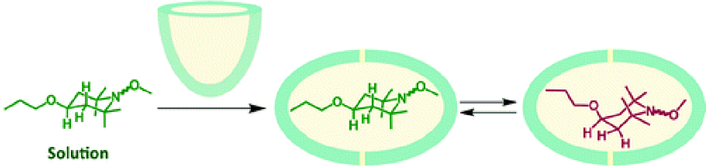
This Account highlights and discusses the recent advances of this research frontier in organometallic photovoltaics. The emerging use of low-bandgap soluble platinum−acetylide polymers in PSCs offers a new and versatile strategy to capture sunlight for efficient solar power generation. Properties of these polyplatinynes—including their chemical structures, absorption coefficients, bandgaps, charge mobilities, accessibility of triplet excitons, molecular weights, and blend film morphologies—critically influence the device performance. Our group has developed a novel strategy that allows for tuning of the optical absorption and charge transport properties as well as the PSC efficiency of these metallopolyynes. The absorbance of these materials can also be tuned to traverse the near-visible and near-infrared spectral regions. Because of the diversity of transition metals available and chemical versatility of the central spacer unit, we anticipate that this class of materials could soon lead to exciting applications in next-generation PSCs and other electronic or photonic devices. Further research in this emerging field could spur new developments in the production of renewable energy.

- Exclusive Photodimerization Reactions of Chromone-2-carboxylic Esters Depending on Reaction Media
  Sakamoto, M.; Yagishita, F.; Kanehiro, M.; Kasashima, Y.; Mino, T.; Fujita, T. *Org. Lett.* **2010**,*12*, 4435-4437.
  Abstract:



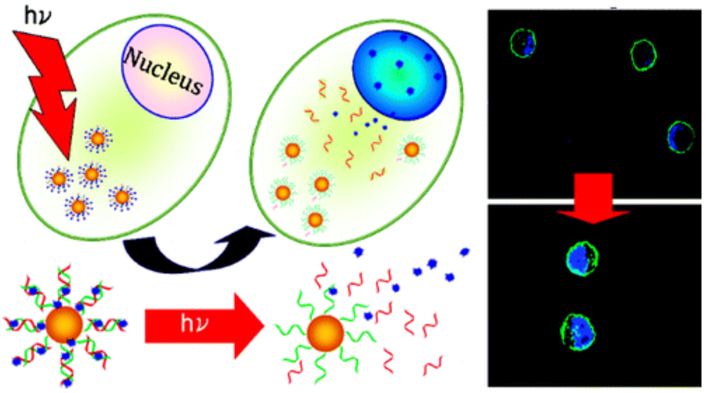
The irradiation of chromone-2-carboxylic esters resulted in the stereo- and regioselective formation of C2 chiral *anti*-HH dimers from the triplet excited state. On the contrary, photolysis in the solid-state gave *anti*-HT dimers exclusively controlled by molecular arrangement in the crystal.

- Chemistry in Confined Spaces: High-Energy Conformer of a Piperidine Derivative is Favored Within a Water-Soluble Capsuleplex
  Porel, M.; Jayaraj, N.; Raghothama, S.; Ramamurthy, V. *Org. Lett.* **2010**,*12*, 4544-4547.
  Abstract:



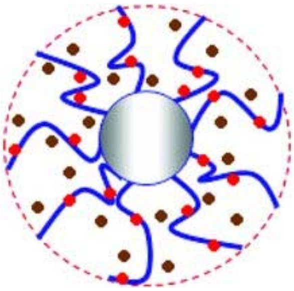
Propyloxy-substituted piperidine in solution adopts a conformation in which its alkoxy group is equatorially positioned. Surprisingly, two conformers of it that do not interconvert in the NMR time scale at room temperature have been found within an octa-acid capsule. The serendipitous finding of the axial conformer of propyloxy-substituted piperidine within a supramolecular capsule highlights the value of confined spaces in physical organic chemistry.

- Visualizing Light-Triggered Release of Molecules Inside Living Cells
  Huschka, R.; Neumann, O.; Barhoumi, A.; Halas, N. J. *Nano Lett.* **2010**, *10*, 4117–4122.
  Abstract:



The light-triggered release of deoxyribonucleic acid (DNA) from gold nanoparticle-based, plasmon resonant vectors, such as nanoshells, shows great promise for gene delivery in living cells. Here we show that intracellular light-triggered release can be performed on molecules that associate with the DNA in a DNA host−guest complex bound to nanoshells. DAPI (4′,6-diamidino-2-phenylindole), a bright blue fluorescent molecule that binds reversibly to double-stranded DNA, was chosen to visualize this intracellular light-induced release process. Illumination of nanoshell-dsDNA-DAPI complexes at their plasmon resonance wavelength dehybridizes the DNA, releasing the DAPI molecules within living cells, where they diffuse to the nucleus and associate with the cell’s endogenous DNA. The low laser power and irradiation times required for molecular release do not compromise cell viability. This highly controlled co-release of nonbiological molecules accompanying the oligonucleotides could have broad applications in the study of cellular processes and in the development of intracellular targeted therapies.

- Nanoscale Organic Hybrid Electrolytes
  Nugent, J. L.; Moganty, S. S.; Archer, L. A. *Adv. Mater.* **2010**, *22*, 3677-3680.
  <u>Abstract:</u>



Nanoscale organic hybrid electrolytes are composed of organic-inorganic hybrid nanostructures, each with a metal oxide or metallic nanoparticle core densely grafted with an ion-conducting polyethylene glycol corona - doped with lithium salt. These materials form novel solvent-free hybrid electrolytes that are particle-rich, soft glasses at room temperature; yet manifest high ionic conductivity and good electrochemical stability above 5V.