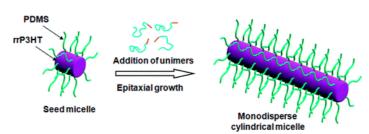
A Successful Chemical Strategy To Induce Oligothiophene Self-Assembly into Fibers with Tunable Shape and Function
Di Maria, F.; Olivelli, P.; Gazzano, M.; Zanelli, A.; Biasiucci, M.; Gigli, G.; Gentili, D.; D'Angelo, P.; Cavallini, M.; Barbarella, G. J. Am. Chem. Soc. 2011, 133, 8654-8661.
<u>Abstract:</u>



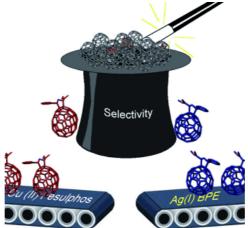
Functional supramolecular architectures for bottom-up organic nano- and microtechnology are a high priority research topic. We discovered a new recognition algorithm, resulting from the combination of thioalkyl substituents and head-to-head regiochemistry of substitution, to induce the spontaneous self-assembly of sulfur overrich octathiophenes into supramolecular crystalline fibers combining high charge mobility and intense fluorescence. The fibers were grown on various types of surfaces either as superhelices or straight rods depending on molecular structure. Helical fibers directly grown on a field effect transistor displayed efficient charge mobility and intrinsic 'memory effect'. Despite the fact that the oligomers did not have chirality centers, one type of hand-helicity was always predominant in helical fibers, due to the interplay of molecular atropisomerism and supramolecular helicity induced by terminal substituents. Finally, we found that the new sulfur overrich oligothiophenes can easily be prepared in high yields through ultrasound and microwave assistance in green conditions.

 Cylindrical Micelles of Controlled Length with a π-Conjugated Polythiophene Core via Crystallization-Driven Self-Assembly Patra, S. K.; Ahmed, R.; Whittell, G. R.; Lunn, D. J.; Dunphy, E. L.; Winnik, M. A.; Manners, I. J. Am. Chem. Soc. 2011, 133, 8842-8845. <u>Abstract:</u>



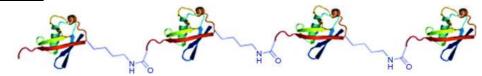
Solution self-assembly of the regioregular polythiophene-based block copolymer poly(3-hexylthiophene)-b-poly(dimethylsiloxane) yields cylindrical micelles with a crystalline P3HT core. Monodisperse nanocylinders of controlled length have been prepared via crystallization-driven self-assembly using seed micelles as initiators.

 Hierarchical Selectivity in Fullerenes: Site-, Regio-, Diastereo-, and Enantiocontrol of the 1,3-Dipolar Cycloaddition to C₇₀ Maroto, E. E.; de Cózar, A.; Filippone, S.; Martín-Domenech, Á.; Suarez, M.; Cossío, F. P.; Martín, N. *Angew. Chem. Int. Ed.* **2011**, *50*, 6060–6064. 2 <u>Abstract:</u>



Make your choice of stereochemistry: The first enantioselective cycloaddition of N-metalated azomethine ylides to the C_{70} molecule affords both pyrrolidino[70]fullerene enantiomers, with *ee* values over 90%, depending on the chiral metal complex used (see picture). The high site- and regioselectivity observed has been accounted for by the nucleophilic and electrophilic Fukui indexes determined by theoretical calculations.

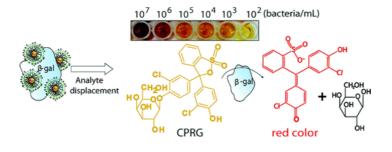
 Total Chemical Synthesis of a 304 Amino Acid K48-Linked Tetraubiquitin Protein Kumar, K. S. A.; Bavikar, S. N.; Spasser, L.; Moyal, T.; Ohayon, S.; Brik, A. Angew. Chem. Int. Ed. 2011, 50, 6137–6141. Abstract:



A new record: The largest chemically synthesized polypeptide composed of 304 residues, which corresponds to folded K48-tetraubiquitin, has been achieved (see scheme). The presented synthetic method could be applied to any of the remaining tetraubiquitin chains, and should ultimately assist ongoing efforts to unravel how the remarkable diversity of ubiquitin signaling is achieved.

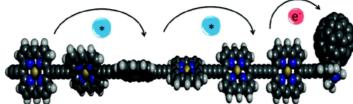
 Colorimetric Bacteria Sensing Using a Supramolecular Enzyme–Nanoparticle Biosensor Miranda, O. R.; Li, X.; Gonzalez, L. G.; Zhu, Z.; Yan, B.; Bunz, U. H. F.; Rotello, V. M. J. Am. Chem. Soc. 2011, 133, 9650–9653.

<u>Abstract:</u>



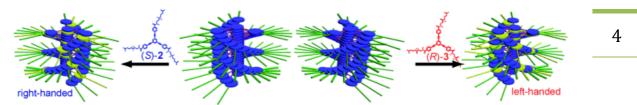
Rapid and sensitive detection of pathogens is a key requirement for both environmental and clinical settings. We report here a colorimetric enzyme–nanoparticle conjugate system for detection of microbial contamination. In this approach, cationic gold nanoparticles (NPs) featuring quaternary amine headgroups are electrostatically bound to an enzyme [β -galactosidase (β -Gal)], inhibiting enzyme activity. Analyte bacteria bind to the NP, which releases the β -Gal and restores its activity, providing an enzyme-amplified colorimetric readout of the binding event. Using this strategy, we have been able to quantify bacteria at concentrations of 1×10^2 bacteria/mL in solution and 1×10^4 bacteria/mL in a field-friendly test strip format.

 Temperature Dependence of Charge Separation and Recombination in Porphyrin Oligomer– Fullerene Donor–Acceptor System
Kahnt, A.; Kàrnbratt, J.; Esdaile, L. J.; Hutin, M.; Sawada, K.; Anderson, H. L.; Albinsson, B. J. Am. Chem. Soc. 2011, 133, 9863–9871.
<u>Abstract:</u>



Electron-transfer reactions are fundamental to many practical devices, but because of their complexity, it is often very difficult to interpret measurements done on the complete device. Therefore, studies of model systems are crucial. Here the rates of charge separation and recombination in donor-acceptor systems consisting of a series of butadiyne-linked porphyrin oligomers (n = 1-4, 6) appended to C₆₀ were investigated. At room temperature, excitation of the porphyrin oligomer led to fast (5–25 ps) electron transfer to C_{60} followed by slower (200–650 ps) recombination. The temperature dependence of the charge-separation reaction revealed a complex process for the longer oligomers, in which a combination of (i) direct charge separation and (ii) migration of excitation energy along the oligomer followed by charge separation explained the observed fluorescence decay kinetics. The energy migration is controlled by the temperaturedependent conformational dynamics of the longer oligomers and thereby limits the quantum yield for charge separation. Charge recombination was also studied as a function of temperature through measurements of femtosecond transient absorption. The temperature dependence of the electrontransfer reactions could be successfully modeled using the Marcus equation through optimization of the electronic coupling (V) and the reorganization energy (λ). For the charge-separation rate, all of the donor-acceptor systems could be successfully described by a common electronic coupling, supporting a model in which energy migration is followed by charge separation. In this respect, the C_{60} -appended porphyrin oligomers are suitable model systems for practical charge-separation devices such as bulk-heterojunction solar cells, where conformational disorder strongly influences the electron-transfer reactions and performance of the device.

 Cooperative Supramolecular Polymerization and Amplification of Chirality in C3-Symmetrical OPE-Based Trisamides
García, F.; Viruela, P. M.; Matesanz, E.; Ortí, E.; Sánchez, L. Chem. Eur. J. 2011, 17, 7755-7759.
<u>Abstract :</u>



Sergeants-and-soldiers experiments demonstrate the amplification of chirality that transforms the racemic mixture of helical columns formed from OPE-based trisamides into enantiomerically enriched helical structures (see scheme). The cooperative supramolecular polymerization of the trisamides is investigated by theoretical calculations and temperature-dependent UV/Vis and CD experiments.

• High-Performance Single-Crystal-Based Organic Field-Effect Transistors from π -Extended Porphyrin Derivatives

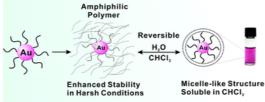
Hoang, M. H.; Kim, Y.; Kim, S. J.; Choi, D. H.; Lee, S. J. *Chem. Eur. J.* **2011**, *17*,7772-7776. <u>Abstract:</u>



Single-crystal OFET: Single-crystals of new porphyrin derivatives TTPH₂ and TTPZn were obtained from slow diffusion of solvents (see graphic). The organic field-effect transistor (OFET) devices based on these single crystals show relatively high mobilities of 6.2×10^{-2} cm2 $\mathbb{P}V^{-1}\mathbb{P}s^{-1}$ for TTPH₂ and 0.32 cm2 $\mathbb{P}V^{-1}\mathbb{P}s^{-1}$ for TTPZn with a high on–off current ratio of >104.

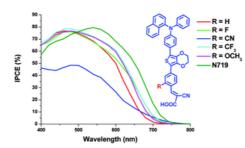
• Highly stable, amphiphilic DNA-encoded nanoparticle conjugates for DNA encoding/decoding applications

Lim, D.-K.; Cui, M.-H.; Nam, J.-M. *J. Mater. Chem.* **2011**, *21*, 9467-9470. <u>Abstract:</u>



We synthesized highly stable, amphiphilic polymer-protected DNA–Au nanoparticle conjugates (DNA–AuNPs) and developed a DNA encoding/decoding strategy using these particles. Here, DNA–AuNPs were encapsulated by amphiphilic poly(*N*-vinyl-2-pyrrolidone) (PVP) to make them more stable and soluble in both organic and aqueous solvents. These particles are stable in a wide range of salt concentrations, pH and temperatures and sustain their stability even after the addition of D,L-dithiothreitol. Finally, this polymer layer was readily removed and particle-modified DNA was decoded *via* the microarrayed chip and dark-field-based AuNP imaging technique.

 Highly efficient triarylene conjugated dyes for sensitized solar cells Chang, Y. J.; Chow, T. J. J. Mater. Chem., 2011, 21, 9523-9531.
<u>Abstract:</u>



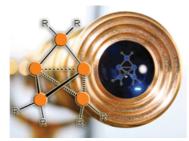
A new series of organic dyes containing a triarylamine donor group, a triarylene-linked bridging moiety, and a cyanoacrylic acid acceptor group were synthesized through a simple procedure in high yields. A selected set of substituents were added onto the phenyl group *ortho* to the cyanoacrylic acid in order to examine their influences on the performance of dye-sensitized solar cells (DSSCs). Their photochemical behaviors were examined under AM1.5 solar condition (100 mW cm⁻²). A typical device made with a compound containing a -CF₃ substituent (PSP-CF₃) displayed a short-circuit current (J_{sc}) 15.16 mA cm⁻², an open-circuit voltage (V_{oc}) 0.68 V, a fill factor (ff) 0.68, corresponding to an overall conversion efficiency of 7.0% and a maximal monochromatic incident photon-to-current conversion efficiency (IPCE) 78%. Their photophysical and electrochemical properties were analyzed with the aid of a time-dependent density functional theory (TDDFT) model with the B3LYP functional. Their HOMO and LUMO energy levels are verified by both electrochemical measurements and theoretical calculations.

Recent advances in [2+2+2] cycloaddition reactions
Domínguez, G.; Pérez-Castells, J. Chem. Soc.Rev. 2011, 40, 3430–3444.
<u>Abstract:</u>



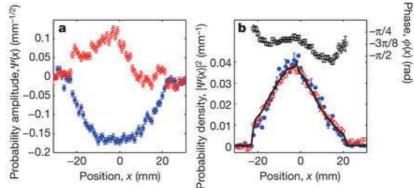
The [2+2+2] cycloaddition is an elegant, atom-efficient and group tolerant process for the synthesis of carbo- and heterocycles, mostly aromatic, involving the formation of several C–C bonds in a single step. Cyclotrimerisation is catalyzed by a variety of organometallic complexes, including more than 15 different metals. The aim of this tutorial review is to point out the most recent advances in this field and to encourage the use of this reaction enroute to complex molecules. After summarizing the most common catalysts and reaction conditions generally used, we survey the mechanistic features currently accepted for this reaction. Section 4 covers the scope of the different [2+2+2] cycloaddition versions starting with the cyclotrimerisation of three triple bonds, including nitriles, with special emphasis on asymmetric reactions that create central, axial or planar chirality. Then, reactions that use double bonds are addressed. Finally, the most outstanding examples of natural products synthesis using [2+2+2] cycloadditions as a key step reported recently are shown.

 New perspectives for "non-classical" molecules: heavy [1.1.1]propellanes of group 14 Nied, D.; Breher, F. Chem. Soc. Rev. 2011, 40, 3455–3466.
<u>Abstract:</u>



Heavy analogues of hydrocarbons intrigue chemists for a number of reasons, not least because they are often fundamentally different from their carbon counterparts and have remained a challenge for both experimentalists and theoreticians for a long time. The appealing properties of [1.1.1]propellanes of group 14 consisting of inverted tetrahedral bridge head atoms can mainly be attributed to the particular bonding between the latter. More than 20 years after the first member of this family has been published, several contributions to this area have impressively extended the spectrum of these so-called main-group biradicaloids. Still in its infancy, further perspectives for these "non-classical" molecules are now arising. In this *tutorial review*, early findings and recent developments in this area are presented. Particular attention is drawn on the relationship of unusual structures and unusual reactivities of main-group element compounds in general and in particular of heavy propellane scaffolds of group 14.

Direct measurement of the quantum wavefunction
Lundeen, J. S.; Sutherland, B.; Patel, A.; Stewart, C.; Bamber, C. Nature 2011, 474, 188-191.
<u>Abstract:</u>



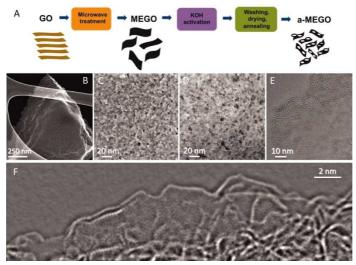
The wavefunction is the complex distribution used to completely describe a quantum system, and is central to quantum theory. But despite its fundamental role, it is typically introduced as an abstract element of the theory with no explicit definition. Rather, physicists come to a working understanding of the wavefunction through its use to calculate measurement outcome probabilities by way of the Born rule. At present, the wavefunction is determined through tomographic methods, which estimate the wavefunction most consistent with a diverse collection of measurements. The indirectness of these methods compounds the problem of defining the wavefunction. Here we show that the wavefunction can be measured directly by the sequential measurement of two complementary variables of the system. The crux of our method is that the first measurement is performed in a gentle way through weak measurement, so as not to invalidate the second. The result is that the real and imaginary components of the wavefunction appear directly on our measurement apparatus. We give an experimental example by directly measuring the transverse spatial wavefunction of a single photon, a task not previously realized by any method. We show that the concept is universal, being applicable to other degrees of freedom of the photon, such as polarization or frequency, and to

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other quantum systems—for example, electron spins, SQUIDs (superconducting quantum interference devices) and trapped ions. Consequently, this method gives the wavefunction a straight forward and general definition in terms of a specific set of experimental operations. We expect it to expand the range of quantum systems that can be characterized and to initiate new avenues in fundamental quantum theory.

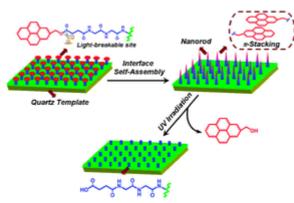
 Carbon-Based Supercapacitors Produced by Activation of Graphene Zhu, Y.; Murali, S.; Stoller, M. D.; Ganesh, K. J.; Cai, W.; Ferreira, P. J.; Pirkle, A.; Wallace, R. M.; Cychosz, K. A.; Thommes, M.; Su, D.; Stach, E. A.; Ruoff, R. S. *Science* 2011, *332*, 1537-1541.

Abstract:



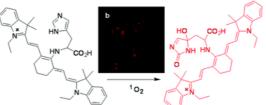
Supercapacitors, also called ultracapacitors or electrochemical capacitors, store electrical charge on high-surface-area conducting materials. Their widespread use is limited by their low energy storage density and relatively high effective series resistance. Using chemical activation of exfoliated graphite oxide, we synthesized a porous carbon with a Brunauer-Emmett-Teller surface area of up to 3100 square meters per gram, a high electrical conductivity, and a low oxygen and hydrogen content. This sp2-bonded carbon has a continuous three-dimensional network of highly curved, atom-thick walls that form primarily 0.6- to 5-nanometer-width pores. Two-electrode supercapacitor cells constructed with this carbon yielded high values of gravimetric capacitance and energy density with organic and ionic liquid electrolytes. The processes used to make this carbon are readily scalable to industrial levels.

 Interface self-assembly to construct vertical peptide nanorods on quartz template Xu, X.-D.; Wang, X.-G.; Lin, B.-B.; Cheng, H.; Zhang, X.-Z.; Zhuo, R.-X. *Chem. Commun.* 2011, 47, 7113-7115.
<u>Abstract:</u>



A rationally designed glycyl–glycine derivative containing a light cleaved pyrenylmethyl ester tail was covalently bound onto the surface of quartz template. The interface self-assembly of this dipeptide induced the formation of chemically bound vertically aligned nanorods (CBVANs) with light sensitivity on the template.

 A selective near-infrared fluorescent probe for singlet oxygen in living cells Xu, K.; Wang, L.; Qiang, M.; Wang, L.; Li, P.; Tang, B. Chem. Commun. 2011, 47, 7386-7388.
<u>Abstract:</u>



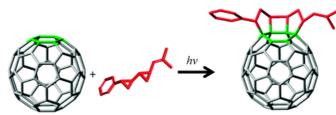
A selective near-infrared fluorescent probe (His–Cy), which features a fast response to ${}^{1}O_{2}$ with high sensitivity and selectivity, was designed, synthesized and applied to bioimaging.

 Efficient Tuning of LUMO Levels of 2,5,8,11-Substituted Perylenediimides via Copper Catalyzed Reactions Battagliarin, G.; Zhao, Y.; Li, C.; Müllen, K. *Org. Lett.* 2011, *13*, 3399–3401. <u>Abstract:</u>



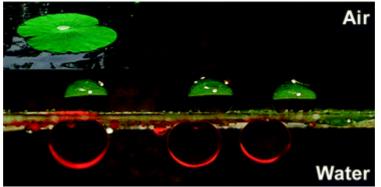
Via one-step copper catalyzed procedures it was possible to synthesize 2,5,8,11-tetrabromo, tetrachloro, and tetracyano derivatives of perylenediimides. Characterization of optical and electrochemical properties of these materials proves substantial enhancement of the electron affinity, with a LUMO level as low as -4.4 eV in the case of the tetracyano perylenediimide.

 Photocycloaddition of Biscyclopropyl Alkenes to C₆₀: An Unprecedented Approach toward *cis*-1 Tricyclic-Fused Fullerene Tzirakis, M. D.; Alberti, M. N.; Orfanopoulos, M. *Org. Lett.* **2011**, *13*, 3364–3367. <u>Abstract:</u>



A novel, simple, and entirely regioselective tandem cycloaddition of biscyclopropyl-substituted alkenes to [60]fullerene has been revealed. This reaction affords *cis*-1 tricyclic-fused organofullerenes bearing the hitherto elusive 5–4–5 fused tricyclic ring system.

Janus interface materials: superhydrophobic air/solid interface and superoleophobic water/solid interface inspired by a lotus leaf
Cheng, Q.; Li, M.; Zheng, Y.; Su, B.; Wang, S.; Jiang, L. Soft Matter 2011, 7, 5948-5951.
<u>Abstract</u>:



We discovered underwater superoleophobicity on the lower side of a lotus leaf, and fabricated Janus interface materials with in-air superhydrophobicity on one side and underwater superoleophobicity on the other side inspired by the Janus feature of the lotus leaf. The ingenious design on lotus leaf surfaces, superhydrophobicity on its upper side and underwater superoleophobicity on its lower side, not only helps us thoroughly understand the special surface wettability of the lotus leaf, but also gives a typical example of multi-functionality in biological systems. This study supplies us with an intelligent strategy to design and create bionic multi-functional interface materials.

PEGylated polyamidoamine dendron-assisted encapsulation of plasmid DNA into in situ forming supramolecular hydrogel
Deng, J.; Luo, Y.; Zhang, L. Soft Matter 2011, 7, 5944-5947.
Abstract:

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 Image: Second

For the first time, PEGylated polyamidoamine dendron was used to condense plasmid DNA (pDNA) into the nanoparticles (polyplexes) and subsequently used to interact with α -cyclodextrin in an

aqueous system. The resultant pDNA polyplexes could be encapsulated into the in situ forming supramolecuar hydrogel and exhibit sustained release and gene transfection properties. 10