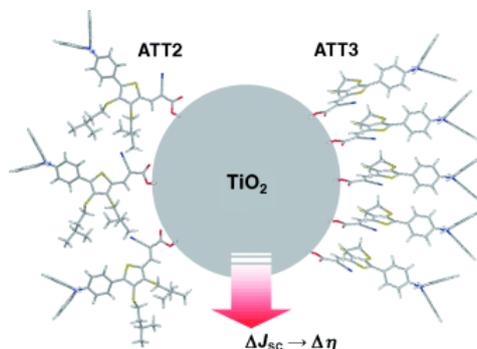


- Influence of Solvent and Bridge Structure in Alkylthio-Substituted Triphenylamine Dyes on the Photovoltaic Properties of Dye-Sensitized Solar Cells
Sakong, C.; Kim, S. H.; Yuk, S. B.; Namgoong, J. W.; Park, S. W.; Ko, M. J.; Kim, D. H.; Hong, K. S.; Kim, J. P. *Chem. Asian J.* **2012**, *7*, 1817–1826.

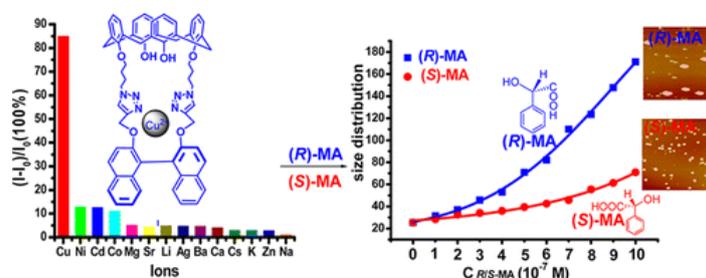
Abstract:



Three new triphenylamine dyes that contain alkylthio-substituted thiophenes with a low bandgap as a π -conjugated bridge unit were designed and synthesized for organic dye-sensitized solar cells (DSSCs). The effects of the structural differences in terms of the position, number, and shape of the alkylthio substituents in the thiophene bridge on the photophysical properties of the dye and the photovoltaic performance of the DSSC were investigated. The introduction of an alkylthio substituent at the 3-position of thiophene led to a decrease in the degree of redshift and the value of the molar extinction coefficient of the charge-transfer band, and the substituent with a bridged structure led to a larger redshift than that of the open-chain structure. The introduction of bulky and hydrophobic side chains decreased the short-circuit photocurrent (J_{sc}), which was caused by the reduced amount of dye adsorbed on TiO_2 . This resulted in a decrease in the overall conversion efficiency (η), even though it could improve the open-circuit voltage (V_{oc}) due to the retardation of charge recombination. Furthermore, the change in solvents for TiO_2 sensitization had a critical effect on the performance of the resulting DSSCs due to the different amounts of dye adsorbed. Based on the optimized dye bath and molecular structure, the ethylene dithio-substituted dye (**ATT3**) showed a prominent solar-to-electricity conversion efficiency of 5.20%.

- Enantioselective Recognition of Mandelic Acid with (R)-1,1-Bi-2-naphthol-Linked Calix[4]arene via Fluorescence and Dynamic Light Scattering
Miao, F.; Zhou, J.; Tian, D.; Li, H. *Org. Lett.* **2012**, *14*, 3572–3575.

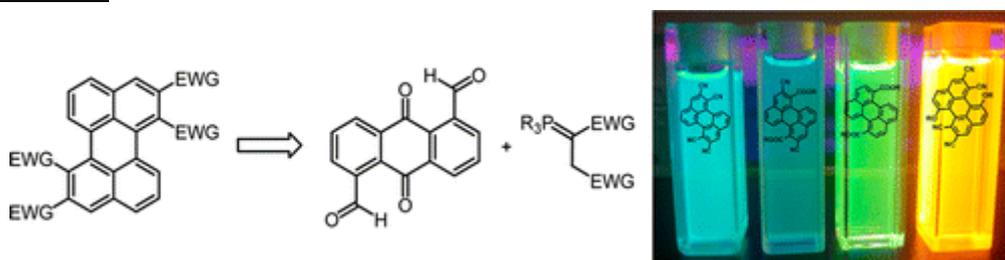
Abstract:



A chiral 1,1-bi-2-naphthol-derived calix[4]arene (**1**) was synthesized via a click reaction. Fluorescence spectra and dynamic light-scattering revealed that $\text{Cu(II)}\text{-1}$ complexes were generated in situ and exhibited remarkable enantioselectivity toward mandelic acid. Using this dynamic light-scattering technique, the detection sensitivity was improved almost 100-fold, with a detection limit of 2.0×10^{-7} M, compared with fluorescent methods.

- New Synthetic Routes to Z-Shape Functionalized Perylenes
Rao, B. B.; Wei, J.-R.; Lin, C.-H. *Org. Lett.* **2012**, *14*, 3640-3643.

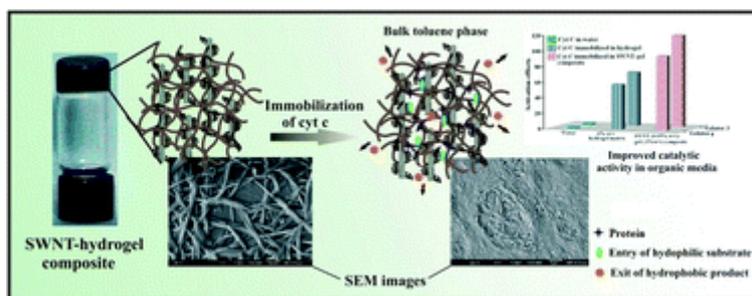
Abstract:



Z-shape (1,2,7,8-tetrasubstituted) perylene derivatives are novel chromophores with great potential in various applications. Yet, the synthetic entry into this class of molecules is hitherto quite limited. In this communication, the synthesis of a series of Z-shape perylene derivatives via a double Wittig–Knoevenagel benzannulation protocol is reported. Preliminary photophysical and electrochemical studies indicate that the frontier orbital energy levels of these new perylene systems are modulated by electronic, regiochemical, and conformational effects.

- Influence of pristine SWNTs in supramolecular hydrogelation: scaffold for superior peroxidase activity of cytochrome c
Kar, T.; Mandal, K.; Kumar Das, P. *Chem. Commun.* **2012**, *48*, 8389-8391.

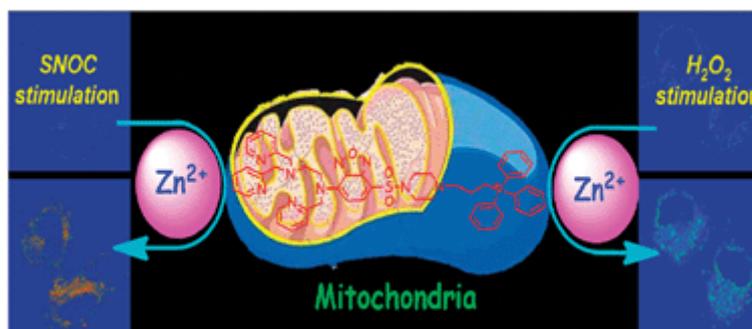
Abstract:



A pristine SWNT-including supramolecular hydrogel of amphiphilic peptide carboxylates was developed. The composite with notable mechanical strength acted as a scaffold for superior biomolecular catalysis in organic media.

- An excitation ratiometric Zn^{2+} sensor with mitochondria-targetability for monitoring of mitochondrial Zn^{2+} release upon different stimulations
Liu, Z.; Zhang, C.; Chen, Y.; He, W.; Guo, Z. *Chem. Commun.* **2012**, *48*, 8365-8367.

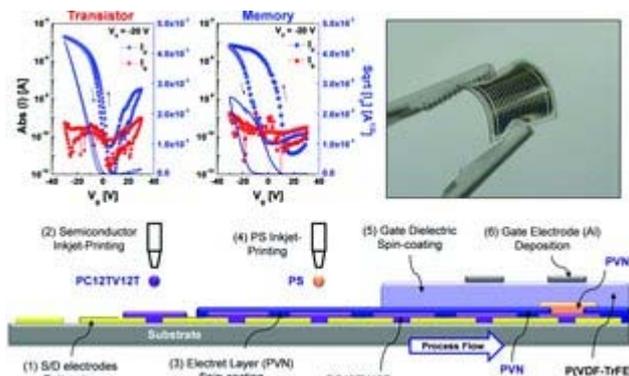
Abstract:



A mitochondria-targeted sensor displays an excitation ratiometric response specifically to Zn^{2+} , and different mitochondrial Zn^{2+} release stimulated by H_2O_2 and SNOC has been clarified.

- High-Performance Top-Gated Organic Field-Effect Transistor Memory using Electrets for Monolithic Printed Flexible NAND Flash Memory
Baeg, K.-J.; Khim, D.; Kim, J.; Yang, B.-D.; Kang, M.; Jung, S.-W.; You, I.-K.; Kim, D.-Y.; Noh, Y.-Y. *Adv. Funct. Mater.* **2012**, *22*, 2915–2926.

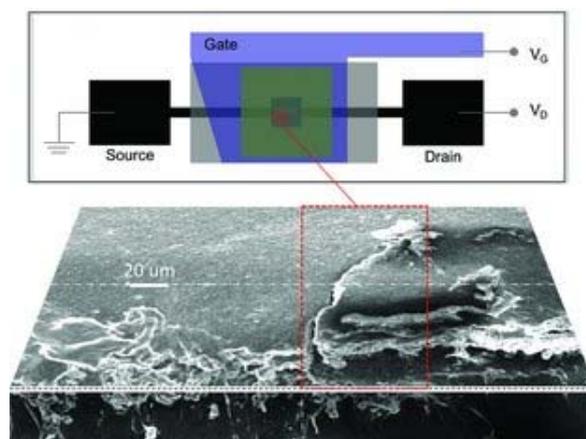
Abstract:



High-performance top-gated organic field-effect transistor (OFET) memory devices using electrets and their applications to flexible printed organic NAND flash are reported. The OFETs based on an inkjet-printed p-type polymer semiconductor with efficiently chargeable dielectric poly(2-vinylnaphthalene) (PVN) and high-k blocking gate dielectric poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) shows excellent non-volatile memory characteristics. The superior memory characteristics originate mainly from reversible charge trapping and detrapping in the PVN electret layer efficiently in low-k/high-k bilayered dielectrics. A strategy is devised for the successful development of monolithically inkjet-printed flexible organic NAND flash memory through the proper selection of the polymer electrets (PVN or PS), where PVN/- and PS/P(VDF-TrFE) devices are used as non-volatile memory cells and ground- and bit-line select transistors, respectively. Electrical simulations reveal that the flexible printed organic NAND flash can be possible to program, read, and erase all memory cells in the memory array repeatedly without affecting the non-selected memory cells.

- Simplified Large-Area Manufacturing of Organic Electrochemical Transistors Combining Printing and a Self-Aligning Laser Ablation Step
Blaudeck, T.; Ersman, P. A.; Sandberg, M.; Heinz, S.; Laiho, A.; Liu, J.; Engquist, I.; Berggren, M.; Baumann, R. R. *Adv. Funct. Mater.* **2012**, *22*, 2939–2948.

Abstract:

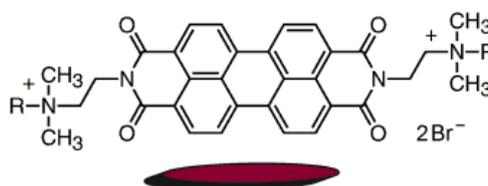
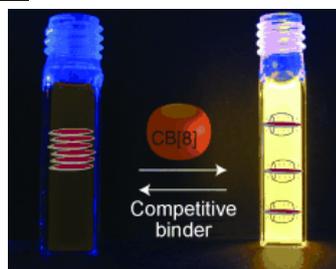


A hybrid manufacturing approach for organic electrochemical transistors (OECTs) on flexible substrates is reported. The technology is based on conventional and digital printing (screen and inkjet printing), laser processing, and post-press technologies. A careful selection of the conductive, dielectric, and semiconductor materials with respect to their optical properties enables a self-aligning pattern formation which results in a significant reduction of the usual registration problems during manufacturing. For the prototype OECTs, based on this technology, on/off ratios up to 600 and switching times of 100 milliseconds at gate voltages in the range of 1 V were obtained.

- Strongly Fluorescent, Switchable Perylene Bis(diimide) Host–Guest Complexes with Cucurbit[8]uril In Water

Biedermann, F.; Elmalem, E.; Ghosh, I.; Nau, W. M.; Scherman, O. A. *Angew. Chem. Int. Ed.* **2012**, *51*, 7739-7743.

Abstract:

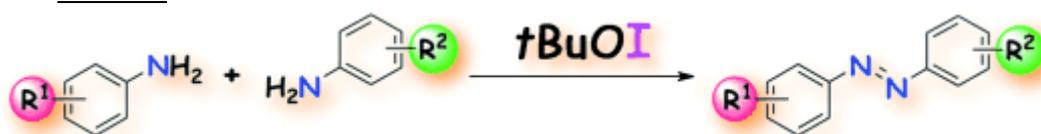


Supramolecular complexation of perylene bis(diimide) (PDI) dyes with the macrocyclic host cucurbit[8]uril (CB[8]) prevents self-aggregation of the dye molecules and enables their use as highly (photo)chemically stable, strongly-emitting fluorophores in water. The complexes are stimuli-responsive to binders and can be electrochemically cycled, leading to reversible on–off fluorescence switching and access to noncovalent formation of higher-order architectures in water.

- Oxidative Dimerization of Aromatic Amines using tBuOI: Entry to Unsymmetric Aromatic Azo Compounds

Takeda, Y.; Okumura, S.; Minakata, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 7804-7808.

Abstract:

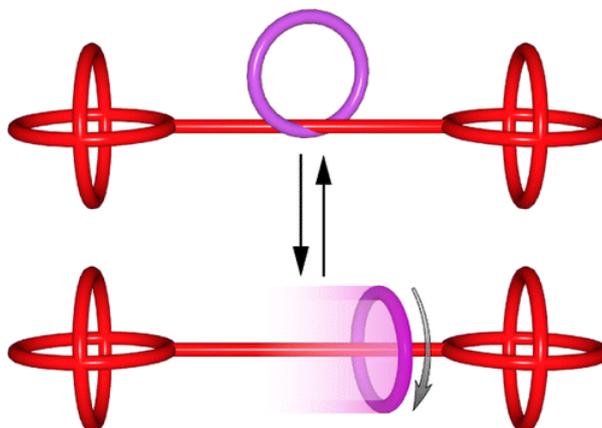


It's all the hype: An oxidative dimerization reaction of aromatic amines utilizing tert-butyl hypoiodite (tBuOI) under mild reaction conditions leads to aromatic azo compounds (see scheme). The method allows access to unsymmetric aromatic azo compounds, which are difficult to prepare by conventional synthetic methods, in a selective manner.

5

- Reversible Light Switch for Macrocycle Mobility in a DNA Rotaxane
Lohmann, F.; Ackermann, D.; Famulok, M. *J. Am. Chem. Soc.* **2012**, *134*, 11884–11887.

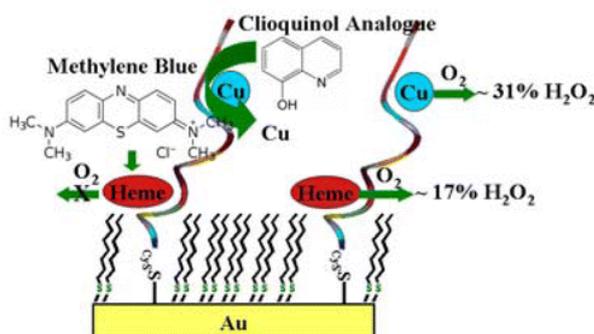
Abstract:



A recent trend in DNA nanotechnology consists of the assembly of architectures with dynamic properties that can be regulated by employing external stimuli. Reversible processes are important for implementing molecular motion into DNA architectures as they allow for the regeneration of the original state. Here we describe two different approaches for the reversible switching of a double-stranded DNA rotaxane architecture from a stationary pseudorotaxane mode into a state with movable components. Both states only marginally differ in their respective topologies but their mechanical properties are fundamentally different. In the two approaches, the switching operation is based on strand-displacement reactions. One of them employs toehold-extended oligodeoxynucleotides whereas in the other one the switching is achieved by light-irradiation. In both cases, multiple back and forth switching between the stationary and the mobile states was achieved in nearly quantitative fashion. The ability to reversibly operate mechanical motion in an interlocked DNA nanostructure opens exciting new avenues in DNA nanotechnology.

- Self-Assembled Monolayers of A β peptides on Au Electrodes: An Artificial Platform for Probing the Reactivity of Redox Active Metals and Cofactors Relevant to Alzheimer's Disease
Pramanik, D.; Sengupta, K.; Mukherjee, S.; Dey, S. G.; Dey, A. *J. Am. Chem. Soc.* **2012**, *134*, 12180–12189.

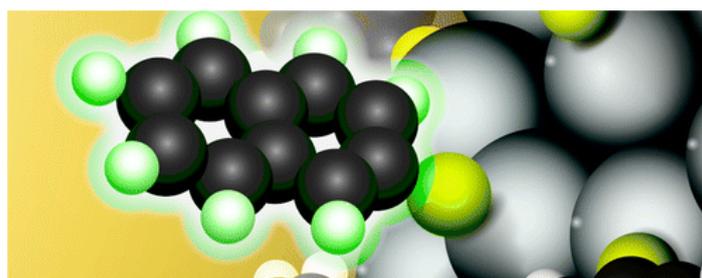
Abstract:



The water-soluble hydrophilic part of human A β peptide has been extended to include a C-terminal cysteine residue. Utilizing the thiol functionality of this cysteine residue, self-assembled monolayers (SAM) of these peptides are formed on Au electrodes. Atomic force microscopy imaging confirms formation of small A β aggregates on the surface of the electrode. These aggregates bind redox active metals like Cu and cofactors like heme, both of which are proposed to generate toxic partially reduced oxygen species (PROS) and play a vital role in Alzheimer's disease. The spectroscopic and electrochemical properties of these Cu and heme bound A β SAM are similar to those reported for the soluble Cu and heme bound A β peptide. Experiments performed on these A β -SAM electrodes clearly demonstrate that (1) heme bound A β is kinetically more competent in reducing O₂ than Cu bound A β , (2) under physiological conditions the reduced Cu site produces twice as much PROS (measured *in situ*) than the reduced heme site, and (3) chelators like clioquinol remove Cu from these aggregates, while drugs like methylene blue inhibit O₂ reactivity of the heme cofactor. This artificial construct provides a very easy platform for investigating potential drugs affecting aggregation of human A β peptides and PROS generation by its complexes with redox active metals and cofactors.

- Long-Lived Charge-Separated States in Ligand-Stabilized Silver Clusters
Pelton, M.; Tang, Y. ; Bakr, O. M.; Stellacci, F. *J. Am. Chem. Soc.* **2012**, *134*, 11856–11859.

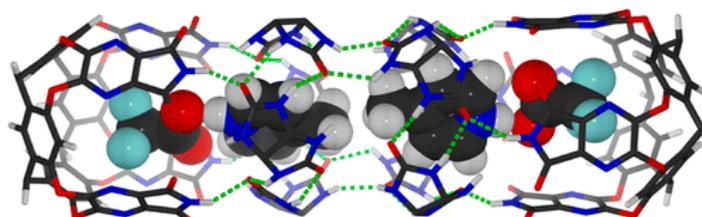
Abstract:



Recently developed synthesis methods allow for the production of atomically monodisperse clusters of silver atoms stabilized in solution by aromatic thiol ligands, which exhibit intense absorption peaks throughout the visible and near-IR spectral regions. Here we investigated the time-dependent optical properties of these clusters. We observed two kinetic processes following ultrafast laser excitation of any of the absorption peaks: a rapid decay, with a time constant of 1 ps or less, and a slow decay, with a time constant that can be longer than 300 ns. Both time constants decrease as the polarity of the solvent increases, indicating that the two processes correspond to the formation and recombination, respectively, of a charge-separated state. The long lifetime of this state and the broad optical absorption spectrum mean that the ligand-stabilized silver clusters are promising materials for solar energy harvesting.

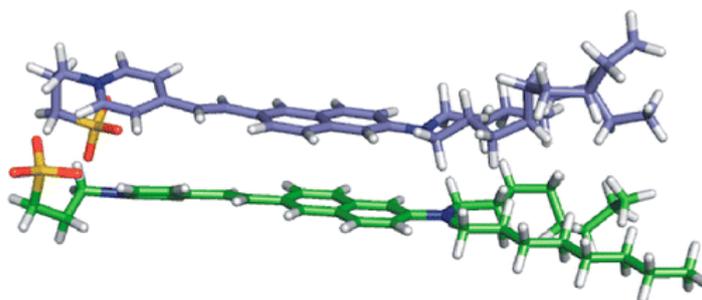
- Encapsulation of Ion Pairs in Extended, Self-Assembled Structures
Taira, T.; Ajami, D.; Rebek, J. Jr. *J. Am. Chem. Soc.* **2012**, *134*, 11971–11973.

Abstract:



Encapsulation of ion pairs in small spaces that are isolated from the medium is expected to result in amplified interactions between the ions. Yet, sequestration of ion pairs in self-assembled capsules is complicated by competition of the acids and bases for binding directly to the assembly components. We describe here a hydrogen-bonded capsule 1.2₈.1 that accommodates two γ -picolines and two acids as ion pairs. The supramolecular structure of the discrete 14-component assembly is characterized by NMR spectroscopy. The structure reveals the acids in the tapered ends of the capsule and γ -picoliniums near the glycoluril spacers in the capsule's center. Similar acid–base ion pairs are also obtained with 4-ethylpyridine, γ -picoline with difluoroacetic acid, and γ -picoline with trifluoromethanesulfonic acid. The ^1H NMR spectrum of the γ -picoline/trifluoroacetic acid ion pair shows a signal at $\delta = 18.7$ ppm, indicating the acidic proton is in contact with both the picoline nitrogen and the trifluoroacetate oxygen. Further details about the unusual structures of ion pairs in small spaces are reported.

- Spectral Properties and Orientation of Voltage-Sensitive Dyes in Lipid Membranes
Matson, M.; Carlsson, N.; Beke-Somfai, T.; Nordén, B. *Langmuir* **2012**, *28*, 10808-10817.
Abstract:

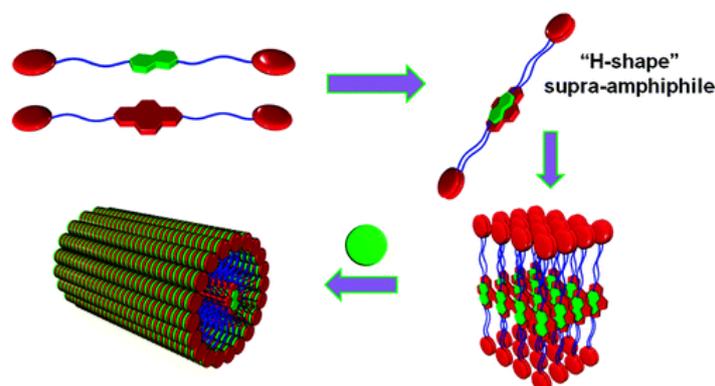


Voltage-sensitive dyes are frequently used for probing variations in the electric potential across cell membranes. The dyes respond by changing their spectral properties: measured as shifts of wavelength of absorption or emission maxima or as changes of absorption or fluorescence intensity. Although such probes have been studied and used for decades, the mechanism behind their voltage sensitivity is still obscure. We ask whether the voltage response is due to electrochromism as a result of direct field interaction on the chromophore or to solvatochromism, which is the focus of this study, as result of changed environment or molecular alignment in the membrane. The spectral properties of three styryl dyes, di-4-ANEPPS, di-8-ANEPPS, and RH421, were investigated in solvents of varying polarity and in model membranes using spectroscopy. Using quantum mechanical calculations, the spectral dependence of monomer and dimer ANEPPS on solvent properties was modeled. Also, the kinetics of binding to lipid membranes and the binding geometry of the probe molecules were found relevant to address. The spectral properties of all three probes were found to be highly sensitive to the local environment, and the probes are oriented nearly parallel with the membrane normal. Slow binding kinetics and scattering in absorption spectra indicate, especially for di-8-ANEPPS, involvement of aggregation. On the basis of the experimental spectra and time-dependent density functional theory calculations, we find that aggregate formation may contribute to the blue-shifts seen for the dyes in decanol and when bound to membrane models. In conclusion, solvatochromic and other intermolecular interactions effects also need to be included when considering electrochromic response voltage-sensitive dyes.

- Self-Assembly of Supra-amphiphiles Based on Dual Charge-Transfer Interactions: From Nanosheets to Nanofibers

Liu, K.; Yao, Y.; Liu, Y.; Wang, C.; Li, Z.; Zhang, X. *Langmuir* **2012**, *28*, 10697-10702.

Abstract:

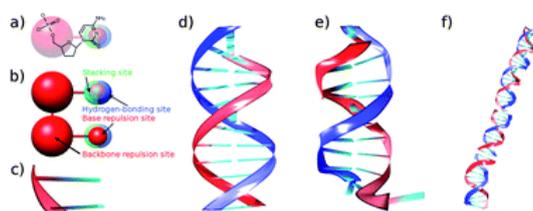


With the elaborate engineering of supra-amphiphiles based on dual charge-transfer interactions, the rational design and programmable transformation of well-defined 1D and 2D nanostructures have been demonstrated. First, H-shaped supra-amphiphiles are successfully obtained on the basis of the directional charge-transfer interactions of naphthalene diimide and naphthalene, which self-assemble in water to form 2D nanosheets. Second, by complexation of the H-shaped supra-amphiphiles with pyrene derivatives, the 2D nanosheets transform into ultralong 1D nanofibers. Therefore, this line of research represents a successful example of supramolecular engineering and has enriched its realm.

- Self-assembly of short DNA duplexes: from a coarse-grained model to experiments through a theoretical link

De Michele, C.; Rovigatti, L.; Bellini, T.; Sciortino, F. *Soft Matter* **2012**, *8*, 8388-8398.

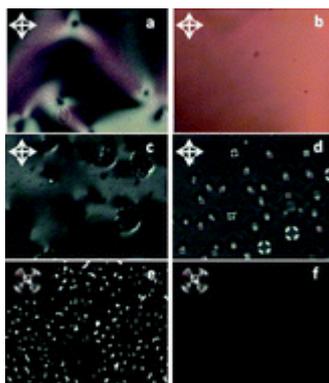
Abstract:



Short blunt-ended DNA duplexes comprising 6 to 20 base pairs self-assemble into polydisperse semi-flexible chains due to hydrophobic stacking interactions between terminal base pairs. Above a critical concentration, which depends on temperature and duplex length, such chains order into liquid crystal phases. Here, we investigate the self-assembly of such double-helical duplexes with a combined numerical and theoretical approach. We simulate the bulk system employing the coarse-grained DNA model recently proposed by Ouldridge *et al.* [*J. Chem. Phys.*, 2011, **134**, 08501]. Then we evaluate the input quantities for the theoretical framework directly from the DNA model. The resulting parameter-free theoretical predictions provide an accurate description of the simulation results in the isotropic phase and theoretical values for the isotropic–nematic phase boundaries which are in line with experimental findings. In addition, the developed theoretical framework makes it possible to provide a route to estimate the stacking free energy.

- Dynamical homeotropic and planar alignments of chromonic liquid crystals

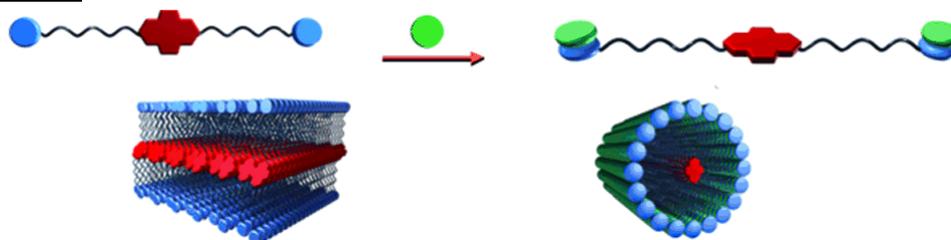
Tone, C. M.; De Santo, M. P.; Buonomenna, M. G.; Golemme, G.; Ciuchi, F. *Soft Matter* **2012**, *8*, 8478-8482.

Abstract:

We report on our latest studies on alignment of chromonic liquid crystals, a special class of molecules which recently attracted the attention of researchers. In particular, we show a detailed study of planar anchoring of disodium cromoglycate (DSCG) and, for the first time in the literature, a stable homeotropic alignment, achieved using a surface property of the alignment layer, *i.e.* the hydrophobicity. Excellent candidates from this point of view are pure polybutadiene (PB) and polydimethylsiloxane (PDMS). In fact, for the former the homeotropic anchoring stabilizes after one day, while for the latter stabilization occurs soon after cooling from the isotropic phase. After a long time both types of alignments (planar and homeotropic) evolve into thermodynamically stable configurations, *i.e.* ribbon structures. An explanation of the behaviour is given.

- From Bola-amphiphiles to Supra-amphiphiles: The Transformation from Two-Dimensional Nanosheets into One-Dimensional Nanofibers with Tunable-Packing Fashion of n-Type Chromophores

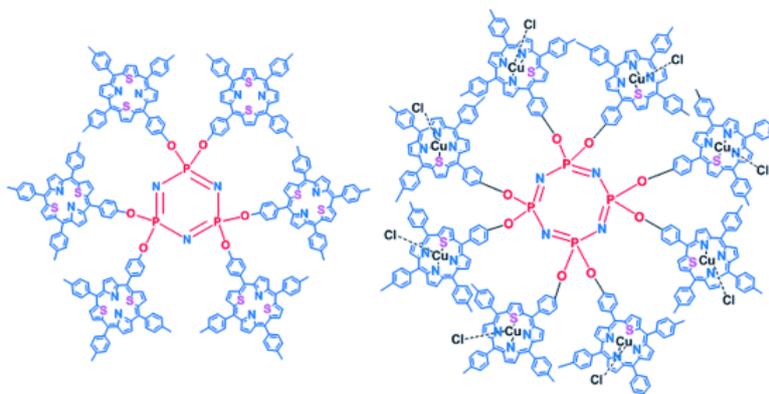
Liu, K.; Yao, Y.; Wang, C.; Liu, Y.; Li, Z.; Zhang, X. *Chem. Eur. J.* **2012**, *18*, 8622–8628.

Abstract:

With a rational design of the supra-amphiphiles, we have successfully demonstrated that not only the dimension of the self-assembled nanostructures, but also the packing fashion of the functional naphthalene diimide (a typical n-type chromophore), can be tuned in a noncovalent way in aqueous solution. Naphthalene diimide is incorporated into a bola-amphiphile as the rigid core, whereas viologen derivatives are used as the hydrophilic head. The bola-amphiphile self-assembles into two-dimensional nanosheets, in which naphthalene diimide adopts a “J-type” aggregation. Water-soluble supramolecular complexation between viologen derivatives and the 8-hydroxypyrene-1, 3, 6-trisulfonic acid trisodium salt is used as a driving force for the formation of the supra-amphiphiles. Upon formation of the supra-amphiphiles, the nanosheets transform into ultralong nanofibers with a close packing of naphthalene diimide. Notably, just by mixing the two building blocks of the supra-amphiphiles in aqueous solution, a dimension-controlled evolution of the nanostructures is formed that leads to a different packing fashion of the n-type functional chromophores, which is facile and environmental friendly.

- Multiporphyrin Arrays on Cyclophosphazene Scaffolds: Synthesis and Studies
Pareek, Y.; Ravikanth, M. *Chem. Eur. J.* **2012**, *18*, 8835–8846.

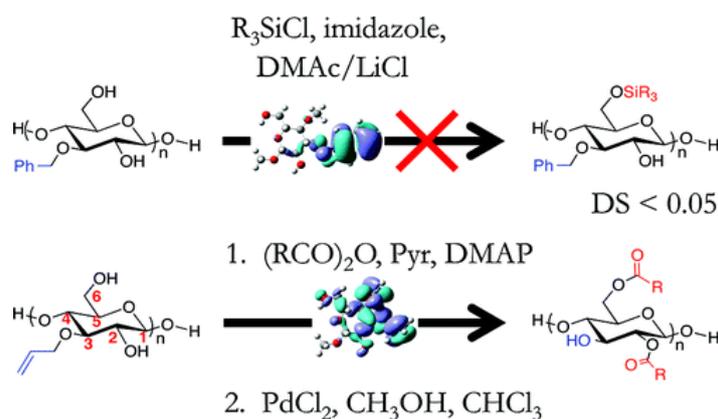
Abstract:



The stable and robust cyclotriphosphazene and cyclotetraphosphazene rings were used as scaffolds to prepare hexa- and octaporphyrin arrays by treating $N_3P_3Cl_6$ and $N_4P_4Cl_8$, respectively, with 5-(4-hydroxyphenyl)-10,15,20-tri(*p*-tolyl)porphyrin (N_4 core) or with its thiaporphyrin analogues (N_3S and N_2S_2 cores) in THF in the presence of Cs_2CO_3 under simple reaction conditions. Thiaporphyrins were examined in addition to the normal porphyrin to tune the electronic properties of the resultant arrays. Observation of the molecular ion peaks in the mass spectra confirmed the molecular structures of the arrays. 1D and 2D NMR techniques were employed to characterize the multiporphyrin arrays in detail. The 1H NMR spectra of the multiporphyrin arrays each show a systematic set of signals, indicating that the porphyrin units are arranged in a symmetrical fashion around the cyclophosphazene rings. All signals in the 1H NMR spectra were assigned with the aid of COSY and NOESY experiments. The protons of each porphyrin unit are subject to upfield and downfield shifts because of the ring-current effects of neighboring porphyrin units. Optical, electrochemical, and fluorescence studies of the arrays indicated that the porphyrin units retain their independent ground- and excited-state characteristics. Cu^{II} and Ni^{II} derivatives of hexaporphyrin and octaporphyrin arrays containing N_4 porphyrin units and N_3S porphyrin units were synthesized, and complete metalation of the arrays was confirmed by their mass spectra and by detailed NMR characterization of the Ni^{II} derivatives of hexa- and octaporphyrin arrays containing N_4 porphyrin units. Electrochemical studies indicated that Cu^{II} and Ni^{II} ions present in the thiaporphyrin units of the arrays can be stabilized in the +1 oxidation state, which is not possible with arrays containing normal porphyrin units.

- Regioselective Synthesis of Cellulose Ester Homopolymers
Xu, D.; Voiges, K.; Elder, T.; Mischnick, P.; Edgar, K. J. *Biomacromolecules* **2012**, *13*, 2195–2201.

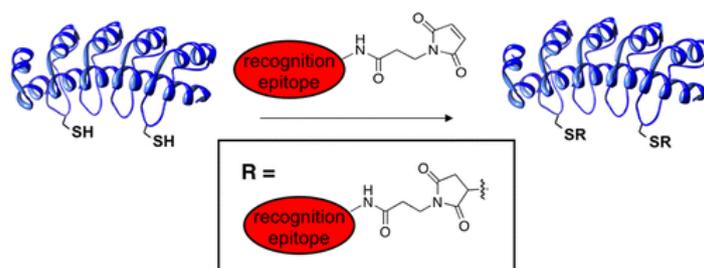
Abstract:



Regioselective synthesis of cellulose esters is extremely difficult due to the small reactivity differences between cellulose hydroxyl groups, small differences in steric demand between acyl moieties of interest, and the difficulty of attaching and detaching many protecting groups in the presence of cellulose ester moieties without removing the ester groups. Yet the synthesis of homopolymers of particular regioselectively substituted anhydroglucose esters is of critical importance to allow us to determine the analytical characteristics of such homopolymers, their structure–property relationships, and to obtain guidance that may ultimately enable identification and synthesis of cellulose derivatives with superior properties for various applications. We report here a new, general synthesis of both cellulose-2,6-*O*-diesters and cellulose-2,6-*A-O*-3-*B-O*-triesters with a high degree of regioselectivity, employing 3-*O*-allylcellulose as a key protected precursor. 3-*O*-Allylcellulose was identified as a protected intermediate with high potential for the synthesis of these derivatives with the aid of molecular modeling of corresponding glucose analogs. We report also the first analytical and structure property studies of these regioselectively substituted cellulose esters.

- Designed Ankyrin Repeat Proteins as Scaffolds for Multivalent Recognition
Hollenbeck, J. J.; Danner, D. J.; Landgren, R. M.; Rainbolt, T. K.; Roberts, D. S. *Biomacromolecules* **2012**, *13*, 1996–2002.

Abstract:

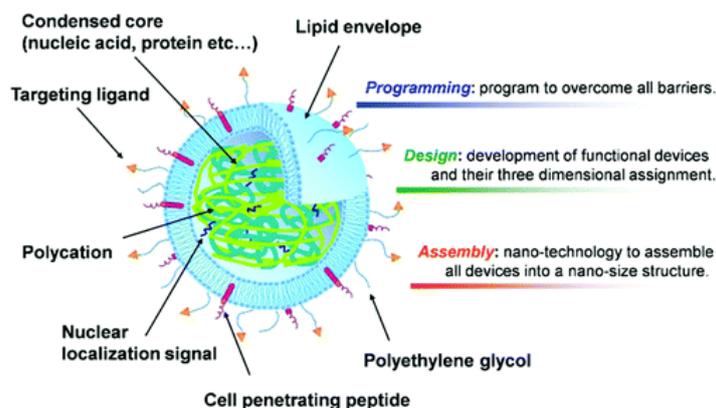


Ankyrin repeat (AR) proteins are composed of tandem repeats of a basic structural motif of ca. 33 amino acid residues that form a β -turn followed by two antiparallel α -helices. Multiple repeats stack together in a modular fashion to form a scaffold that is ideally suited for the presentation of multiple functional groups and/or recognition elements. Here we describe a biosynthetic strategy that takes advantage of the modular nature of these proteins to generate multivalent ligands that are both chemically homogeneous and structurally well-defined. Glycosylated AR proteins cluster the tetrameric lectin concanavalin A (Con A) at a rate that is comparable to the rate of Con A aggregation mediated by globular protein conjugates and variable density linear polymers. Thus, AR proteins define a new class of multivalent ligand scaffolds that have significant potential application in the study and control of a variety of multivalent interactions.

- A Multifunctional Envelope-type Nanodevice for Use in Nanomedicine: Concept and Applications

Nakamura, T.; Akita, H.; Yamada, Y.; Hatakeyama, H.; Harashima, H. *Acc. Chem. Res.* **2012**, *45*, 1113–1121.

Abstract:

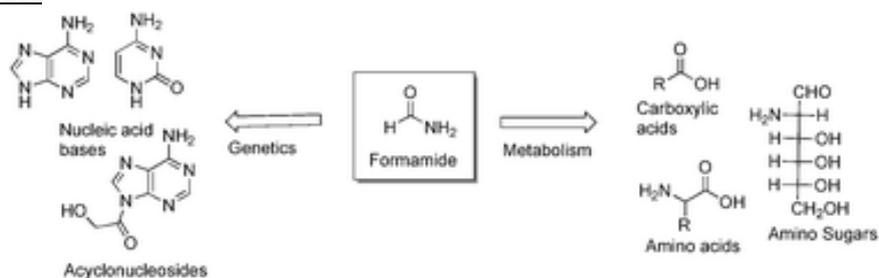


We have developed a new delivery system, a multifunctional envelope-type nanodevice (MEND) based on “Programmed Packaging.” In this new concept of packaging, multifunctional nanodevices are integrated into a nanocarrier system according to a program designed to overcome all barriers during the course of biodistribution and intracellular trafficking. In this Account, we introduce our method for delivering nucleic acids or proteins to intracellular sites of action such as the cytosol, nucleus, and mitochondria and for targeting selective tissues in vivo via systemic administration of the nanodevices.

- Genetics first or metabolism first? The formamide clue

Saladino, R.; Botta, G.; Pino, S.; Costanzo, G.; Di Mauro, E. *Chem. Soc. Rev.* **2012**, *41*, 5526–5565.

Abstract:



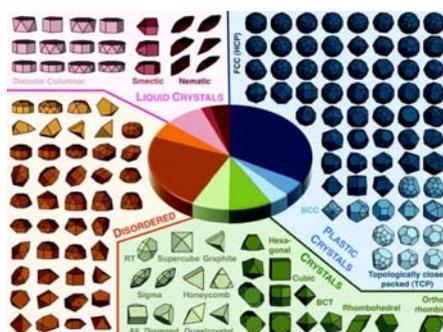
Life is made of the intimate interaction of metabolism and genetics, both built around the chemistry of the most common elements of the Universe (hydrogen, oxygen, nitrogen, and carbon). The transmissible interaction of metabolic and genetic cycles results in the hypercycles of organization and de-organization of chemical information, of living and non-living. The origin-of-life quest has long been split into several attitudes exemplified by the aphorisms “genetics-first” or “metabolism-first”. Recently, the opposition between these approaches has been solved by more unitary theoretical and experimental frames taking into account energetic, evolutionary, proto-metabolic and environmental aspects. Nevertheless, a unitary and simple chemical frame is still needed that could afford both the precursors of the synthetic pathways eventually leading to RNA and to the key components of the central metabolic cycles, possibly connected with the synthesis of fatty acids. In order to approach

the problem of the origin of life it is therefore reasonable to start from the assumption that both metabolism and genetics had a common origin, shared a common chemical frame, and were embedded under physical–chemical conditions favourable for the onset of both. The singleness of such a prebiotically productive chemical process would partake of Darwinian advantages over more complex fragmentary chemical systems. The prebiotic chemistry of formamide affords in a single and simple physical–chemical frame nucleic bases, acyclonucleosides, nucleotides, biogenic carboxylic acids, sugars, amino sugars, amino acids and condensing agents. Thus, we suggest the possibility that formamide could have jointly provided the main components for the onset of both (pre)genetic and (pre)metabolic processes. As a note of caution, we discuss the fact that these observations only indicate possible solutions at the level of organic substrates, not at the systemic chemical level.

- Predictive Self-Assembly of Polyhedra into Complex Structures

Damasceno, P. F.; Engel, M.; Glotzer, S. C. *Science* **2012**, *337*, 453-457.

Abstract:

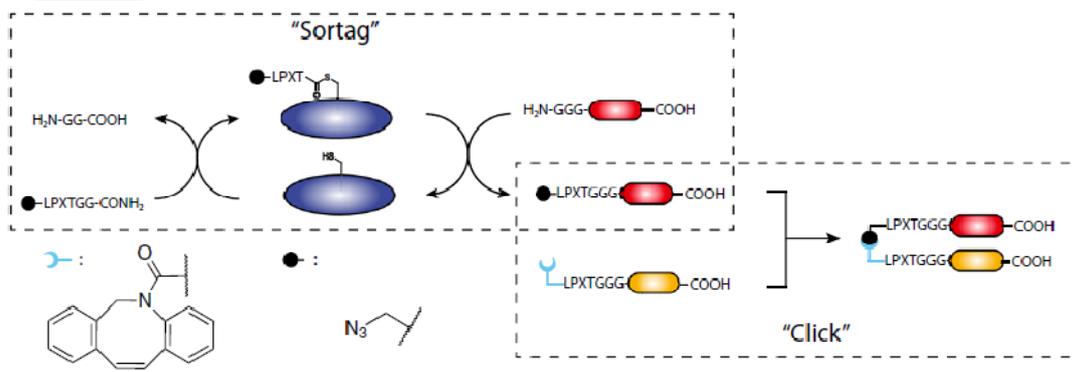


Predicting structure from the attributes of a material's building blocks remains a challenge and central goal for materials science. Isolating the role of building block shape for self-assembly provides insight into the ordering of molecules and the crystallization of colloids, nanoparticles, proteins, and viruses. We investigated 145 convex polyhedra whose assembly arises solely from their anisotropic shape. Our results demonstrate a remarkably high propensity for thermodynamic self-assembly and structural diversity. We show that from simple measures of particle shape and local order in the fluid, the assembly of a given shape into a liquid crystal, plastic crystal, or crystal can be predicted.

- Preparation of unnatural N-to-N and C-to-C protein fusions

Witte, M. D.; Cragnolini, J. J.; Dougan, S. K.; Yoder, N. C.; Popp, M. W.; Ploegh, H. L. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 11993-11998.

Abstract:

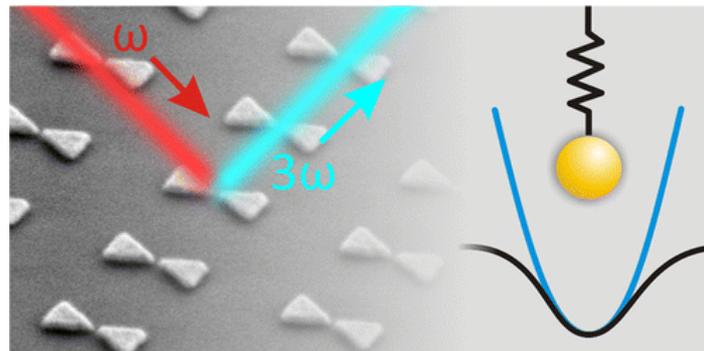


Standard genetic approaches allow the production of protein composites by fusion of polypeptides in head-to-tail fashion. Some applications would benefit from constructions that are genetically

impossible, such as the site-specific linkage of proteins via their N or C termini, when a remaining free terminus is required for biological activity. We developed a method for the production of N-to-N and C-to-C dimers, with full retention of the biological activity of both fusion partners and without inflicting chemical damage on the proteins to be joined. We use sortase A to install on the N or C terminus of proteins of interest the requisite modifications to execute a strain-promoted copper-free cycloaddition and show that the ensuing ligation proceeds efficiently. Applied here to protein-protein fusions, the method reported can be extended to connecting proteins with any entity of interest.

- Quantitative Modeling of the Third Harmonic Emission Spectrum of Plasmonic Nanoantennas
Hentschel, M.; Utikal, T.; Giessen, H.; Lippitz, M. *Nano Letters* **2012**, *12*, 3778-3782.

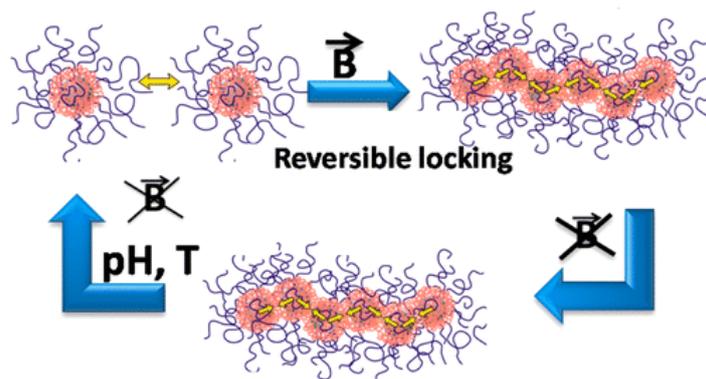
Abstract:



Plasmonic dimer nanoantennas are characterized by a strong enhancement of the optical field, leading to large nonlinear effects. The third harmonic emission spectrum thus depends strongly on the antenna shape and size as well as on its gap size. Despite the complex shape of the nanostructure, we find that for a large range of different geometries the nonlinear spectral properties are fully determined by the linear response of the antenna. We find excellent agreement between the measured spectra and predictions from a simple nonlinear oscillator model. We extract the oscillator parameters from the linear spectrum and use the amplitude of the nonlinear perturbation only as scaling parameter of the third harmonic spectra. Deviations from the model only occur for gap sizes below 20 nm, indicating that only for these small distances the antenna hot spot contributes noticeable to the third harmonic generation. Because of its simplicity and intuitiveness, our model allows for the rational design of efficient plasmonic nonlinear light sources and is thus crucial for the design of future plasmonic devices that give substantial enhancement of nonlinear processes such as higher harmonics generation as well as difference frequency mixing for plasmonically enhanced terahertz generation.

- Field-Directed Self-Assembly with Locking Nanoparticles
Motornov, M.; Malynych, S. Z.; Pippalla, D. S.; Zdyrko, B.; Royter, H.; Roiter, Y.; Kahabka, M.; Tokarev, A.; Tokarev, I.; Zhulina, E.; Kornev, K. G.; Luzinov, I.; Minko, S. *Nano Letters* **2012**, *12*, 3814-3820.

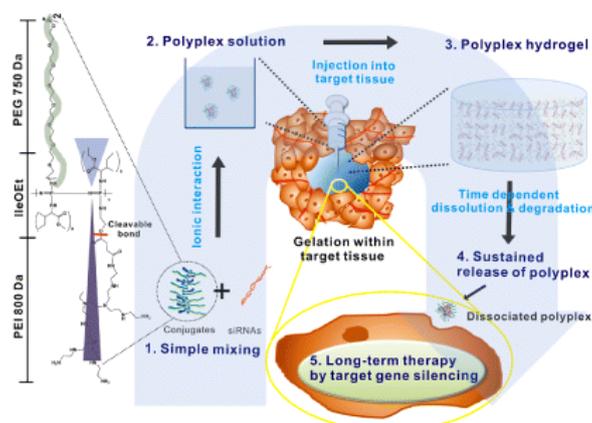
Abstract:



A reversible locking mechanism is established for the generation of anisotropic nanostructures by a magnetic field pulse in liquid matrices by balancing the thermal energy, short-range attractive and long-range repulsive forces, and dipole–dipole interactions using a specially tailored polymer shell of nanoparticles. The locking mechanism is used to precisely regulate the dimensions of self-assembled magnetic nanoparticle chains and to generate and disintegrate three-dimensional (3D) nanostructured materials in solvents and polymers.

- **Injectable Polyplex Hydrogel for Localized and Long-Term Delivery of siRNA**
Kim, Y.-M.; Park, M.-R.; Song, S.-C. *ACS Nano* **2012**, *6*, 5757-5766.

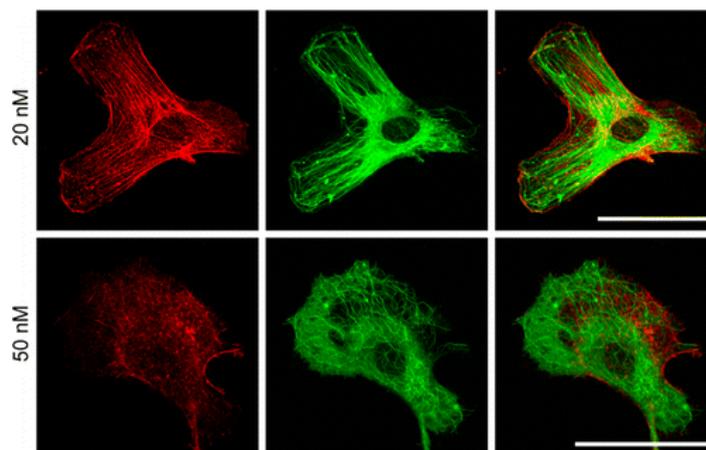
Abstract:



Here, we describe a concept for localized and long-term delivery of short interfering RNA (siRNA) using an injectable polyplex hydrogel possessing thermosensitivity and biodegradability properties. We prepared a low molecular weight polyethyleimine–poly(organophosphazene) conjugate as a thermosensitive and cationic polymer that has a cleavable ester linkage. The conjugates formed about 100 nm sized polyplexes with siRNAs, and the polyplex solution turned into a polyplex hydrogel at body temperature *via* a hydrophobic interaction. We injected the polyplex hydrogel with siRNA of cyclin B1, an essential protein for controlling the cell cycle, into the tumor xenograft model. Polyplexes were slowly released from the polyplex hydrogel by dissolution and degradation, allowing an *in vivo* antitumor effect *via* cyclin B1 gene silencing for 4 weeks with only a single injection.

- **Cytotoxic Effects of Gold Nanoparticles: A Multiparametric Study**
Soenen, S. J.; Manshian, B.; Montenegro, J. M.; Amin, F.; Meermann, B.; Thiron, T.; Cornelissen, M.; Vanhaecke, F.; Doak, S.; Parak, W. J.; De Smedt, S.; Braeckmans, K. *ACS Nano* **2012**, *6*, 5767-5783.

Abstract:

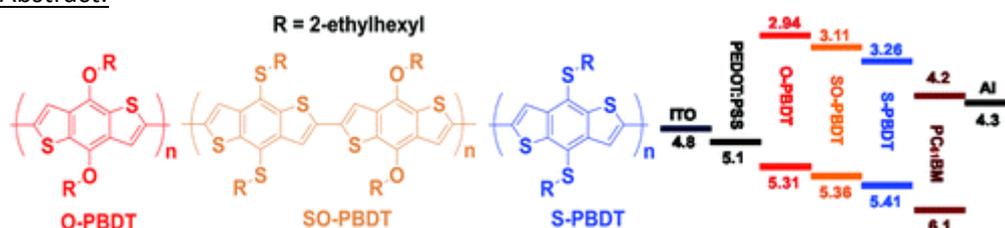


The *in vitro* labeling of therapeutic cells with nanoparticles (NPs) is becoming more and more common, but concerns about the possible effects of the NPs on the cultured cells are also increasing. In the present work, we evaluate the effects of poly(methacrylic acid)-coated 4 nm diameter Au NPs on a variety of sensitive and therapeutically interesting cell types (C17.2 neural progenitor cells, human umbilical vein endothelial cells, and PC12 rat pheochromocytoma cells) using a multiparametric approach. Using various NP concentrations and incubation times, we performed a stepwise analysis of the NP effects on cell viability, reactive oxygen species, cell morphology, cytoskeleton architecture, and cell functionality. The data show that higher NP concentrations (200 nM) reduce cell viability mostly through induction of reactive oxygen species, which was significantly induced at concentrations of 50 nM Au NPs or higher. At these concentrations, both actin and tubulin cytoskeleton were deformed and resulted in reduced cell proliferation and cellular differentiation. In terms of cell functionality, the NPs significantly impeded neurite outgrowth of PC12 cells up to 20 nM concentrations. At 10 nM, no significant effects on any cellular parameter could be observed. These data highlight the importance of using multiple assays to cover the broad spectrum of cell–NP interactions and to determine safe NP concentrations and put forward the described protocol as a possible template for future cell–NP interaction studies under comparable and standardized conditions.

- Enhanced and Tunable Open-Circuit Voltage using Dialkylthio Benzo[1,2-b:4,5-b']dithiophene in Polymer Solar Cells

Lee, D.; Hubijar, E.; Kalaw, G. J. D.; Ferraris, J. P. *Chem. Mater.* **2012**, *24*, 2534–2540.

Abstract:

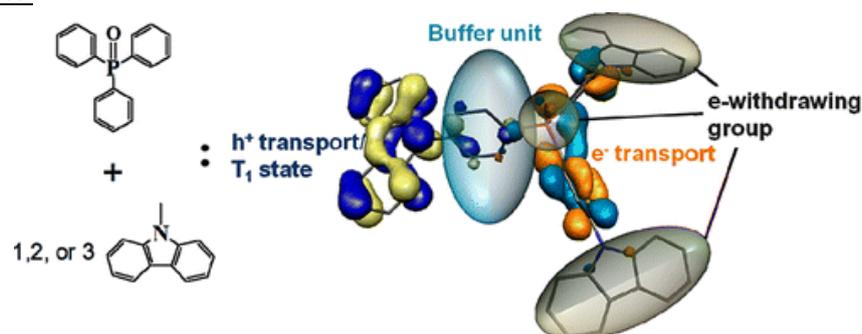


In this study, we explore the effect of the dialkoxy and dithioalkoxy side chains on the benzo [1,2-b:4,5-b']dithiophene (BDT) unit by comparing the O-BDT homopolymer (O-PBDT), S-BDT homopolymer (S-PBDT), and S-BDT-alt-O-BDT copolymer (SO-PBDT) by computational calculations and experimental results. The polymers were prepared by Pd-catalyzed Stille coupling. Additionally, hole mobility and film morphology were studied by fabricating organic field effect transistors (OFETs) and using TappingMode AFM, respectively. The photovoltaic properties of the polymers were

measured from fabricated PSC devices. The replacement of the alkoxy (–OR) groups with thioalkoxy (–SR) groups lowered the HOMO energy level of the conjugated polymers from 5.31 to 5.41 eV, and consequently enhanced V_{oc} , while still preserving the excellent properties offered by the BDT-based polymers. Especially, high V_{oc} of 0.99 V was achieved from S-PBDT polymer based PSC with up to 4.0% of PCE, which is one of the highest efficiencies reported from a homopolymer-based PSC without thermal/solvent annealing or incorporated additives.

- Electronic Structure of Carbazole-Based Phosphine Oxides as Ambipolar Host Materials for Deep Blue Electrophosphorescence: A Density Functional Theory Study
Kim, D.; Zhu, L.; Brédas, J.-L. *Chem. Mater.* **2012**, *24*, 2604–2610.

Abstract:



We report the results of Density Functional Theory calculations on a series of carbazole-based phosphine oxides that experimental data have shown to be promising ambipolar host molecules for deep blue electrophosphorescence. The hosts under investigation contain either 1, 2, or 3 carbazole subunits attached to the phenyl rings of a triphenylphosphoryl group, with the carbazoles acting as hole transporters/acceptors and the triphenylphosphoryl groups as electron transporters/acceptors. The results underline that, in addition to the strong inductive effect of the phosphoryl groups, the LUMO of these hosts is further stabilized by the molecular orbital interactions among the phenyl rings of the triphenylphosphoryl group, which is modulated by the electron-withdrawing inductive effects of the carbazole subunits. The lowest triplet state of the hosts correspond to localized transitions within the carbazole units, which leads to a high triplet energy on the order of 3 eV. We describe the important buffer role of the phenyl rings in preventing the phosphoryl moiety from negatively affecting the hole-accepting characteristics and high triplet energies of the carbazole units.