

- Modular Synthesis of Polyferrocenylsilane Block Copolymers by Cu-Catalyzed Alkyne/Azide “Click” Reactions

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Zhang, M.; Rugar, P. A.; Feng, C.; Lin, K.; Lunn, D. J.; Oliver, A.; Nunns, A.; Whittell, G. R.; Manners, I.; Winnik, M. A. *Macromolecules* **2013**, *46*, 1296-1304.

Abstract:

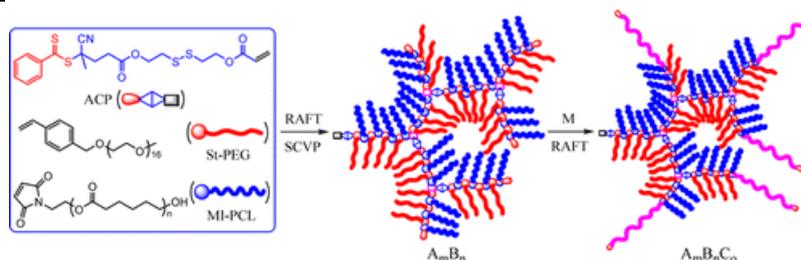


This paper reports a new synthetic strategy for the preparation of polyferrocenylsilane (PFS) block copolymers. The block copolymers were prepared by Cu-catalyzed alkyne/azide cycloaddition of two homopolymer precursors that allows access to new functional PFS block copolymers (e.g., polyferrocenylsilane-block-poly(N-isopropylacrylamide)) (PFS-b-PNIPAM)). Trimethylsilyl-protected, alkyne-terminated PFS homopolymer was first prepared via living anionic polymerization, terminating living PFS with commercially available 4-[(trimethylsilyl)ethynyl]benzaldehyde. Subsequent deprotection of the trimethylsilyl group with NaOMe yielded the ethynyl-terminated PFS (ω -alkyne-PFS). This method should be readily applicable to other polymers prepared by living anionic polymerization. Subsequently, non-PFS homopolymers containing a complementary “clickable” azide functional group were synthesized either by anionic polymerization, modification of a commercially available polymer, or atom transfer radical polymerization via two different approaches. In an azide postpolymerization modification approach, polystyrene (PS) and poly(methyl methacrylate) (PMMA) were functionalized by azide substitution of the terminal halide after ATRP. Alternatively, the azide moiety was incorporated into the ATRP initiator prior to polymerization, e.g., to give PNIPAM-N₃ and poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA-N₃). Finally, the alkyne-terminated PFS segment and the azide functionalized counter block were coupled through the formation of a 1,2,3-triazole ring. In this report, PFS-b-PNIPAM, PFS-b-PDMAEMA, PFS-b-PS, PFS-b-PMMA, PFS-b-polydimethylsiloxane, and PFS-block-poly(ethylene oxide) have been synthesized via this convenient modular protocol in high yield and high purity.

- Synthesis and Properties of Multicleavable Amphiphilic Dendritic Comblike and Toothbrushlike Copolymers Comprising Alternating PEG and PCL Grafts

Zhang, M.; Liu, H.; Shao, W.; Miao, K.; Zhao, Y. *Macromolecules* **2013**, *46*, 1325-1336.

Abstract:

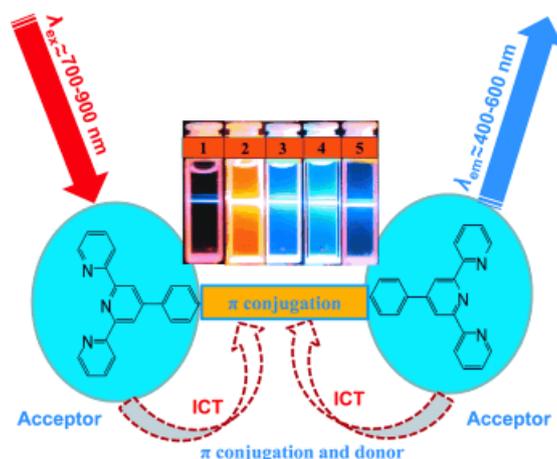


Facile construction of novel functional dendritic copolymers by combination of self-condensing vinyl polymerization, sequence-controlled copolymerization and RAFT process was presented. RAFT copolymerization of a disulfide-linked polymerizable RAFT agent and equimolar feed ratio of styrenic and maleimidic macromonomers afforded multicleavable $A_m B_n$ dendritic comblike copolymers with

alternating PEG (A) and PCL (B) grafts, and a subsequent chain extension polymerization of styrene, tert-butyl acrylate, methyl methacrylate, and N-isopropylacrylamide gave A_mB_nCo dendritic toothbrushlike copolymers. $(PEG)_m(PCL)_n$ copolymers obtained were of adjustable molecular weight, relatively low polydispersity ($PDI = 1.10-1.32$), variable CTA functionality ($f_{CTA} = 4.3-7.5$), and similar segment numbers of PEG and PCL grafts, evident from 1H NMR and GPC-MALLS analyses. Their branched architecture was confirmed by (a) reduction-triggered degradation, (b) decreased intrinsic viscosities and Mark-Houwink-Sakurada exponent than their "linear" analogue, and (c) lowered glass transition and melting temperatures and broadened melting range as compared with normal A_mB_n comblike copolymer. In vitro drug release results revealed that the drug release kinetics of the disulfide-linked A_mB_n copolymer aggregates was significantly affected by macromolecular architecture, end group and reductive stimulus. These stimuli-responsive and biodegradable dendritic copolymer aggregates had a great potential as controlled delivery vehicles.

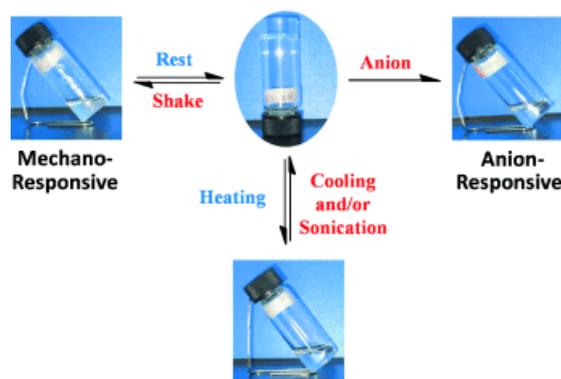
- Large Two-Photon Absorption of Terpyridine-Based Quadrupolar Derivatives: Towards their Applications in Optical Limiting and Biological Imaging
He, T.; Lim, Z. B.; Ma, L.; Li, H.; Rajwar, D.; Ying, Y.; Di, Z.; Grimsdale, A. C.; Sun, H. *Chem. Asian J.* **2013**, *8*, 564-571.

Abstract:



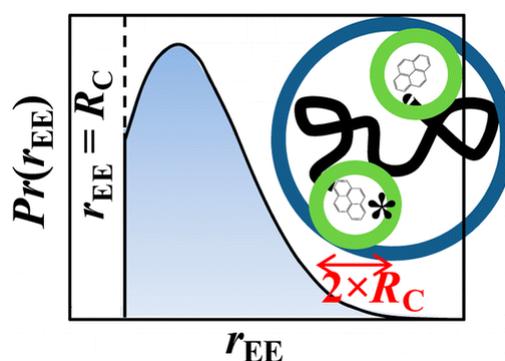
Developing organic chromophores with large two-photon absorption (TPA) in both organic solvents and aqueous media is crucial owing to their applications in solid-state photonic devices and biological imaging. Herein, a series of novel terpyridine-based quadrupolar derivatives have been synthesized. The influences of electron-donating group, type of conjugated bridge, as well as solvent polarity on the molecular TPA properties have been investigated in detail. In contrast to the case in organic solvents, bis(thienyl)-benzothiadiazole as a rigid conjugated bridge will completely quench molecular two-photon emission in aqueous media. However, the combination of alkylcarbazole as the donor and bis(styryl)benzene as a conjugation bridge can enlarge molecular TPA cross-sections in both organic solvent and aqueous media. The reasonable two-photon emission brightness for the organic nanoparticles of chromophores **3-5** in the aqueous media, prepared by the reprecipitation method, enables them to be used as probes for in vivo biological imaging.

- Beyond Perylene Diimides—Diazaperopyrenium Dications as Chameleonic Nanoscale Building Blocks
Liu, J.; Feng, Y.; Liu, Z.-X.; Yan, Z.-C.; He, Y.-M.; Liu, C.-Y.; Fan, Q.-Y. *Chem. Asian J.* **2013**, *8*, 572-581.

Abstract:

A new class of poly(benzyl ether) dendrimers, decorated in their cores with N-Boc-protected 1,2-diphenylethylenediamine groups, were synthesized and fully characterized. It was found that the gelation capability of these dendrimers was highly dependent on dendrimer generation, and the second-generation dendrimer (*R,R*)-G₂DPENBoc proved to be a highly efficient organogelator. A number of experiments (SEM, TEM, FTIR spectroscopy, ¹H NMR spectroscopy, rheological measurements, UV/Vis absorption spectroscopy, CD, and XRD) revealed that these dendritic molecules self-assembled into elastically interpenetrating one-dimensional nanostructures in organogels. The hydrogen bonding, π - π , and solvophobic interactions were found to be the main driving forces for formation of the gels. Most interestingly, these dendritic organogels exhibited smart multiple-stimulus-responsive behavior upon exposure to environmental stimuli such as temperature, anions, and mechanical stress.

- Probing the Hydrophobic Interactions of a Series of Pyrene End-Labeled Poly(ethylene oxide)s in Aqueous Solution Using Time-Resolved Fluorescence
Chen, S.; Duhamel, J. *Langmuir* **2013**, *29*, 2821–2834.

Abstract:

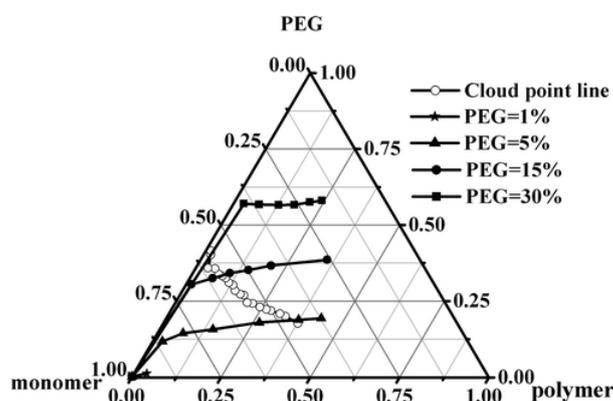
The hydrophobic association of a series of poly(ethylene oxide)s covalently labeled at both ends with pyrene (PEO(X)-Py2 where X represents the number average molecular weight (Mn) of the PEO chains equal to 2, 5, 10, and 16.5 kDa) in aqueous solutions was investigated at different polymer concentrations (CP) using steady-state and time-resolved fluorescence measurements. Phase separation was observed with PEO(2 kDa)-Py2 and PEO(5 kDa)-Py2 samples at high CP. The steady-state fluorescence spectra showed that the ratios of excimer-to-monomer fluorescence intensities (IE/IM) of all PEO samples remained constant when CP was below 4×10^{-5} M and decreased dramatically with increasing PEO chain length due to a decrease in intramolecular pyrene excimer formation. The IE/IM ratio in this regime was found to scale as $Mn^{-2.3 \pm 0.2}$. For $CP > 4 \times 10^{-5}$ M, pyrene excimer is formed by both intra- and intermolecular interactions and the IE/IM ratio increases

linearly with increasing CP except for PEO(2 kDa)-Py2 which undergoes phase separation. The decays obtained at various polymer concentrations were fitted according to a “sequential model” (SM) which assumes that the pyrene excimer is formed in a sequential manner. The molar fractions of all excited pyrene species and the rate constants for pyrene excimer formation were determined from the global analysis of the monomer and excimer fluorescence decays. The fraction of pyrenes that formed excimer from ground-state pyrene aggregates (fE0) was found to increase with CP in the regime where the pyrene excimer is formed both intra- and intermolecularly and decrease with Mn in the regime where the pyrene excimer is formed only intramolecularly. The fraction of pyrene pendants subject to hydrophobic interactions were used to determine the hydrophobic capture radius (Rc) of pyrene in water from the distribution of PEO end-to-end distances. Rc was found to equal 2.2 ± 0.2 nm using fE0.

- Role of Poly(ethylene glycol) in Surfactant-Free Emulsion Polymerization of Styrene and Methyl Methacrylate

Shi, Y.; Shan, G.; Shang, Y. *Langmuir* **2013**, *29*, 3024–3033.

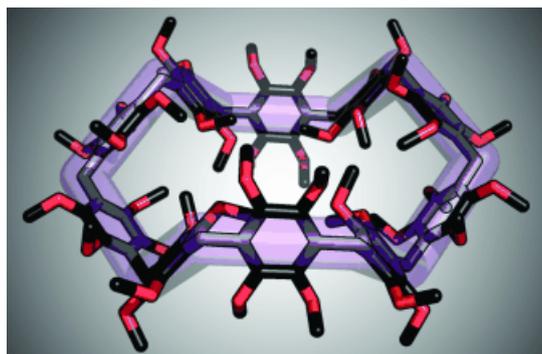
Abstract:



Through zeta potential and surface tension measurements and a series of polymerization experiments, the role of poly(ethylene glycol) (PEG) in the process of surfactant-free polymerization of styrene (St)/methyl methacrylate (MMA) has been investigated experimentally. Nanoscale and stable copolymer particles were formed after an abnormal process, in which the nucleation and growth of particles was different from that in previously proposed mechanisms. It has been observed that PEG can exist in both the monomer and the aqueous phases at high temperature. PEG in the aqueous phase could form copolymer particles with a loose structure, making them prone to enter the monomer phase. Entry of these copolymer particles into the monomer phase would introduce excess PEG. From the ternary phase diagram, a solubility curve could be delineated in the ternary system of PEG/monomer/copolymer. The system used the ternary solubility property to regenerate copolymer particles in the monomer phase, which maintained their morphology until the end of the polymerization. At the end, consumption of the monomer resulted in the volume contraction of the particles, and the surface potential increased. This increasing potential is a driving force to prevent particles from stacking, leading to the formation of nanoscale and stable particles.

- Asararenes—A Family of Large Aromatic Macrocycles
Schneebeli, S. T.; Cheng, C.; Hartlieb, K. J.; Strutt, N. L.; Sarjeant, A. A.; Stern, C. L.; Stoddart, J. F. *Chem. Eur. J.* **2013**, *19*, 3860–3868.

Abstract:

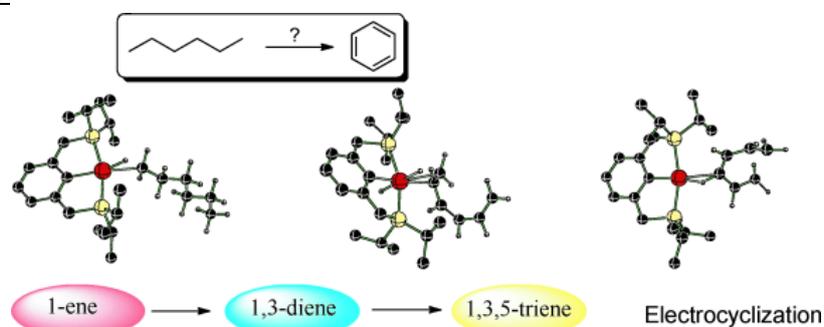


We announce the establishment of a new family of macrocycles—the asararenes, which are based on *para*-methylene linked “asarol methyl ether” (1,2,4,5-tetramethoxybenzene) units. Macrocycles with 6–12 aromatic units have been synthesized and isolated in a single step from asarol methyl ether and paraformaldehyde. Even larger rings, with up to 15 asarol methyl ether units, have been observed by high-resolution mass spectrometry. Single-crystal X-ray structures of asar[6]-, asar[7]-, asar[8]-, asar[9]-, asar[10]- and asar[11]arene highlight the diverse structural features of this family of macrocycles. While the cavities of the asar[6–8]arene macrocycles are mostly filled with methoxyl groups, the asar[9]- and asar[10]arene rings contain accessible cavities and self-assemble into infinite channels filled with solvent molecules in the solid state. These solid-state structures highlight the potential of this family of macrocycles for a wide range of potential applications.

- On the Mechanism of the Dehydroaromatization of Hexane to Benzene by an Iridium Pincer Catalyst

Thawani, A.; Rajeev, R.; Sunoj, R. B. *Chem. Eur. J.* **2013**, *19*, 4069–4077.

Abstract:

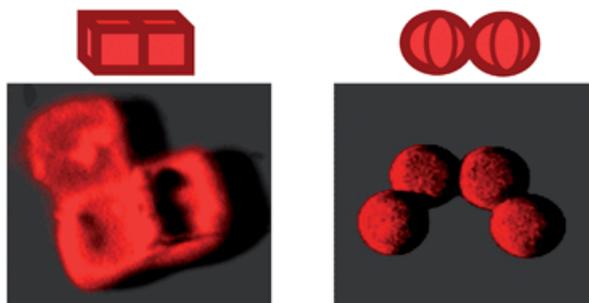


The developments in the area of transition-metal pincer complexes have opened up new avenues for conversion of saturated hydrocarbons to more useful aromatic compounds under homogeneous reaction conditions. In the backdrop of an interesting series of conversions of unbranched alkanes to benzene, toluene, and xylene (known as the BTX family aromatics) reported by Goldman and co-workers (*Nature Chem.* **2011**, *3*, 167), we herein present a comprehensive mechanistic picture obtained by using density functional computations. The reaction involves an iridium–PCP–pincer-catalyzed dehydroaromatization of hexane to benzene (in which $\text{PCP}=\eta^3\text{-C}_6\text{H}_3(i\text{PrP})_2\text{-1,3}$) by using *tert*-butylethylene (TBE) as a sacrificial acceptor. The most energetically preferred pathway for a sequence of dehydrogenations is identified to begin with a terminal C—H bond activation of *n*-hexane leading to the formation of hex-1-ene. Although the initial dehydrogenation of *n*-hexane was found to be endergonic, the accompanying exoergic hydrogenation of TBE to *tert*-butylethane (TBA) compensates the energetics to keep the catalytic cycle efficient. Subsequent dehydrogenations provide a hexa-1,3-diene and then a hexa-1,3,5-triene. The pincer bound triene is identified to undergo cyclization to

furnish cyclohexadiene. Eventually, dehydrogenation of cyclohexa-1,3-diene offers benzene. In the most preferred pathway, the Gibbs free energy barrier for cyclization leading to the formation of cyclohexa-1,3-diene is found to exhibit the highest barrier (21.7 kcal mol⁻¹).

- Assembly of the anisotropic microcapsules in aqueous dispersions
Lisunova, M.; Dorokhin, A.; Holland, N.; Shevchenko, V. V.; Tsukruk, V. V. *Soft Matter* **2013**, *9*, 3651-3660.

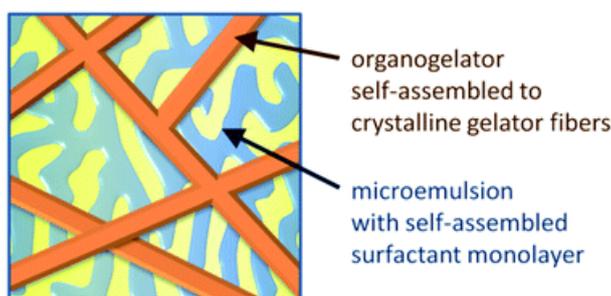
Abstract:



The assembly of cubic hollow microcapsules in an aqueous buffer solution had been studied in comparison with the traditional spherical microcapsules with both microcapsules assembled from identical components and having identical surface charges. We observed that the cubic microcapsules mainly form the highly compacted “boxed” clusters with a number of microcubes controlled by ionic strengths in a sharp contrast to the spherical microcapsules for which the random branched chain structures are generally favored. The assembled spherical microcapsules create a large number of openings with extensive internal surface areas while the cubic microcapsules build close, compacted aggregates with densely packed units. The dimensions of the “boxed” clusters from similarly charged cubic microcapsules are greatly stabilized by strong facet-to-facet interactions and can be tuned in a wide range by changing ionic strength. The chain spherical microcapsules are mobile and capable of reconfiguration due to the lower hydrophobic energy of attraction in contrast to compact, stable aggregates of cubic microcapsules. The dramatic differences in assembly of microcapsules *with similar nature but different shapes* point that the aggregation behavior in such dispersions might be dominated by shape geometry and alternation of facet-to-facet interactions.

- Studying orthogonal self-assembled systems: phase behaviour and rheology of gelled microemulsions
Laupheimer, M.; Jovic, K.; Antunes, F. E.; da Graca Martins Miguel, M.; Stubenrauch, C. *Soft Matter* **2013**, *9*, 3661-3670.

Abstract:



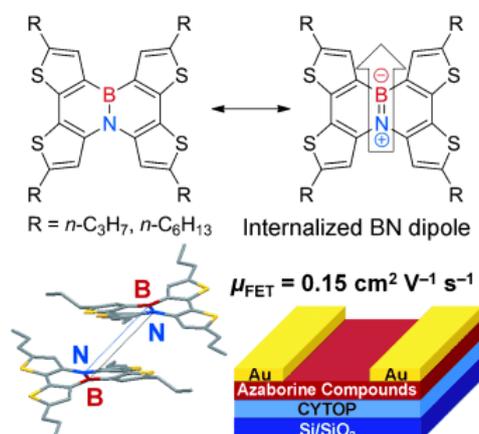
Microemulsions in a gelled form are desirable for applications like topical and transdermal drug delivery as they enable local application and enhanced residence times of the drug. One method for

gelling microemulsions consists of adding an appropriate low molecular weight gelator. Although our group has reported this method before, a systematic study on the nature and properties of such gelled microemulsions has been missing to date. In this paper we present phase studies and rheology results which demonstrate that microemulsions gelled by a low molecular weight gelator are orthogonal self-assembled systems. We studied the gelled microemulsion H₂O-*n*-decane/12-hydroxyoctadecanoic acid (12-HOA)-tetraethylene glycol monodecyl ether (C₁₀E₄) with 1.5 wt%, 2.5 wt% and 5.0 wt% of the low molecular weight organogelator 12-HOA. We found that the phase boundaries of the gelled microemulsion are about 6 K below those of the non-gelled "base" microemulsion H₂O-*n*-decane-C₁₀E₄, irrespective of the gelator concentration. Moreover, we detected by differential scanning calorimetry and rheological measurements a sol-gel boundary about 20 K below that of the respective binary gel *n*-decane/12-HOA. Both temperature shifts are not surprising considering that (a) 12-HOA is surface active, thus influencing the microemulsion's phase behaviour and (b) that the microemulsion can be treated as a solvent in a 12-HOA gel which influences the gel properties. The general phase behaviour of both base systems, however, is indeed maintained in the gelled microemulsion. For the rheological properties we found, accordingly, perfect agreement with the respective binary gel. Thus, our data clearly substantiate that gelled microemulsions are orthogonal self-assembled systems.

- Azaborine Compounds for Organic Field-Effect Transistors: Efficient Synthesis, Remarkable Stability, and BN Dipole Interactions

Wang, X.-Y.; Lin, H.-R.; Lei, T.; Yang, D.-C.; Zhuang, F.-D.; Wang, J.-Y.; Yuan, S.-C.; Pei, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 3117–3120.

Abstract:

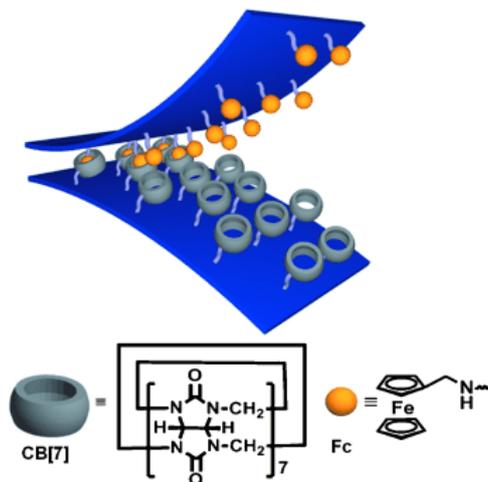


Boron–nitrogen units were incorporated into thiophene-fused polycyclic aromatic compounds. Organic field-effect transistors based on these azaborine compounds were fabricated, demonstrating a novel engineering concept of organic semiconductors and providing opportunities of a broad class of BN-containing compounds for application in future organic electronic devices (see picture; μ_{FET} =hole mobility).

- Supramolecular Velcro for Reversible Underwater Adhesion

Ahn, Y.; Jang, Y.; Selvapalam, N.; Yun, G.; Kim, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 3140–3144.

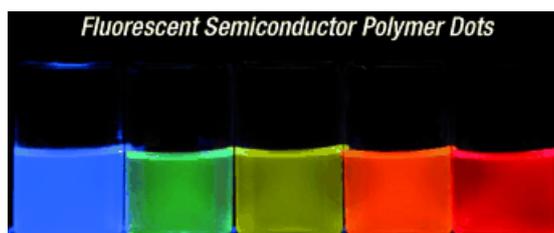
Abstract:



Sticky job: Excellent underwater adhesion with remarkable mechanical and chemical reversibility has been demonstrated with a supramolecular velcro using host–guest chemistry and multivalent interactions (see scheme). Silicon surfaces (blue) functionalized with cucurbit[7]uril (CB[7]) hosts and aminomethylferrocene (Fc) guests adhere under water because of their extraordinarily high affinity.

- Highly Fluorescent Semiconducting Polymer Dots for Biology and Medicine
Wu, C.; Chiu, D. T. *Angew. Chem. Int. Ed.* **2013**, *52*, 3086–3109.

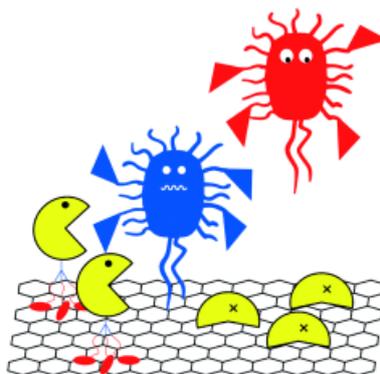
Abstract:



On the dot: As a new class of fluorescent nanoparticles, semiconducting polymer dots, exhibit excellent characteristics such as extraordinary fluorescence brightness, fast emission rates, excellent photostability, nonblinking, and nontoxicity. This review summarizes recent advances of the polymer dots as nanoparticle labels for biological and medical applications (see figure).

- Preservation of Antibody Selectivity on Graphene by Conjugation to a Tripod Monolayer
Mann, J. A.; Alava, T.; Craighead, H. G.; Dichtel, W. R. *Angew. Chem. Int. Ed.* **2013**, *52*, 3177–3180.

Abstract:



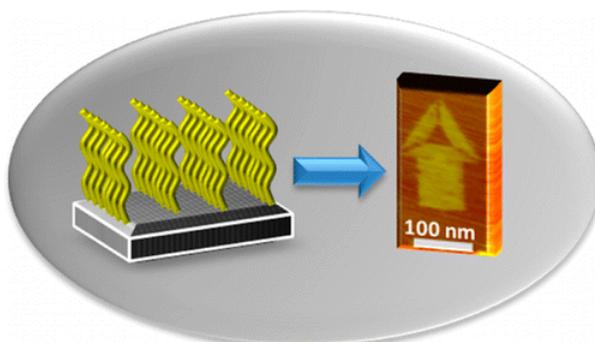
Three is a magic number: Antibodies adsorbed on bare graphene lose their ability to recognize

antigens. However, this obstacle can be overcome by the conjugation of these antibodies to self-assembled monolayers of a tripodal compound (see picture).

- One-Pot Assembly of a Hetero-dimeric DNA Origami from Chip-Derived Staples and Double-Stranded Scaffold

Marchi, A. N.; Saaem, I.; Tian, J.; LaBean, T. H. *ACS Nano* **2013**, 7, 903-910.

Abstract:

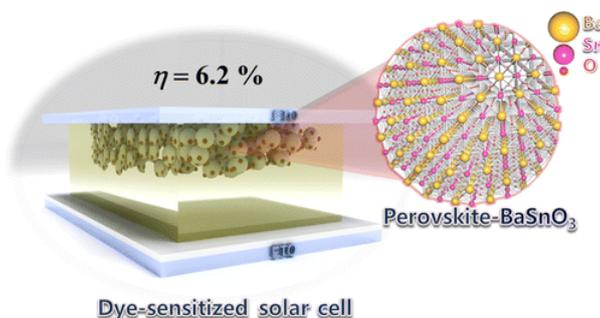


Although structural DNA nanotechnology, and especially scaffolded DNA origami, hold great promise for bottom-up fabrication of novel nanoscale materials and devices, concerns about scalability have tempered widespread enthusiasm. Here we report a single-pot reaction where both strands of double-stranded M13-bacteriophage DNA are simultaneously folded into two distinct shapes that then heterodimerize with high yield. The fully addressable, two-dimensional heterodimer DNA origami, with twice the surface area of standard M13 origami, formed in high yield (81% of the well-formed monomers undergo dimerization). We also report the concurrent production of entire sets of staple strands by a unique, nicking strand-displacement amplification (nSDA) involving reusable surface-bound template strands that were synthesized in situ using a custom piezoelectric inkjet system. The combination of chip-based staple strand production, double-sized origami, and high-yield one-pot assembly markedly increases the useful scale of DNA origami.

- Improved Quantum Efficiency of Highly Efficient Perovskite BaSnO₃-Based Dye-Sensitized Solar Cells

Shin, S. S.; Kim, J. S.; Suk, J. H.; Lee, K. D.; Kim, D. W.; Park, J. H.; Cho, I. S.; Hong, K. S.; Kim, J. Y. *ACS Nano* **2013**, 7, 1027-1035.

Abstract:



Ternary oxides are potential candidates as an electron-transporting material that can replace TiO₂ in dye-sensitized solar cells (DSSCs), as their electronic/optical properties can be easily controlled by manipulating the composition and/or by doping. Here, we report a new highly efficient DSSC using perovskite BaSnO₃ (BSO) nanoparticles. In addition, the effects of a TiCl₄ treatment on the physical, chemical, and photovoltaic properties of the BSO-based DSSCs are investigated. The TiCl₄ treatment

was found to form an ultrathin TiO₂ layer on the BSO surface, the thickness of which increases with the treatment time. The formation of the TiO₂ shell layer improved the charge-collection efficiency by enhancing the charge transport and suppressing the charge recombination. It was also found that the TiCl₄ treatment significantly reduces the amount of surface OH species, resulting in reduced dye adsorption and reduced light-harvesting efficiency. The trade-off effect between the charge-collection and light-harvesting efficiencies resulted in the highest quantum efficiency (i.e., short-circuit photocurrent density), leading to the highest conversion efficiency of 5.5% after a TiCl₄ treatment of 3 min (cf. 4.5% for bare BSO). The conversion efficiency could be increased further to 6.2% by increasing the thickness of the BSO film, which is one of the highest efficiencies from non-TiO₂-based DSSCs.

- Retention or Inversion in Stereospecific Nickel-Catalyzed Cross-Coupling of Benzylic Carbamates with Arylboronic Esters: Control of Absolute Stereochemistry with an Achiral Catalyst

Harris, M. R.; Hanna, L. E.; Greene, M. A.; Moore, C. E.; Jarvo, E. R. *J. Am. Chem. Soc.* **2013**, *135*, 3303–3306.

Abstract:

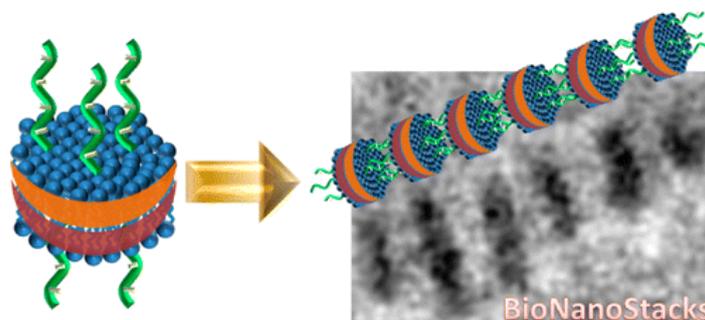


Stereospecific coupling of benzylic carbamates and pivalates with aryl- and heteroarylboronic esters has been developed. The reaction proceeds with selective inversion or retention at the electrophilic carbon, depending on the nature of the ligand. Tricyclohexylphosphine ligand provides the product with retention, while an N-heterocyclic carbene ligand provides the product with inversion.

- Reversible Assembly of Stacked Membrane Nanodiscs with Reduced Dimensionality and Variable Periodicity

Beales, P. A.; Geerts, N.; Inampudi, K. K.; Shigematsu, H.; Wilson, C. J.; Vanderlick, T. K. *J. Am. Chem. Soc.* **2013**, *135*, 3335–3338.

Abstract:

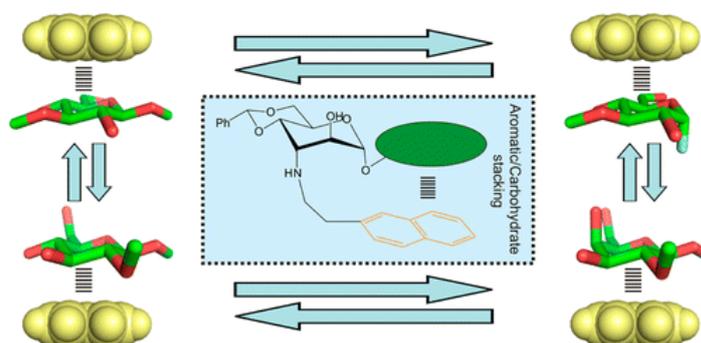


We demonstrate the self-organization of quasi-one-dimensional nanostructures with periodic features using nature's primary three building blocks: lipids, DNA, and proteins. The periodicity of these "BioNanoStacks" is controllable through selection of the length of the DNA spacers. We show that BioNanoStacks can be reversibly assembled and disassembled through thermal melting of the DNA duplex, where the melting transition temperature is controllable not just by the DNA sequence

and salt concentration, but also by the lipid composition within these superstructures. These novel materials may find applications in fields such as templated nanomaterial assembly, tissue-engineering scaffolds, or therapeutic delivery systems. Well-established techniques for chemical modification of biomolecules will also provide a broad platform for adaption and remodeling of these structures to provide optimal features for the required application.

- A Dynamic Combinatorial Approach for the Analysis of Weak Carbohydrate/Aromatic Complexes: Dissecting Facial Selectivity in CH/ π Stacking Interactions
Santana, A. G.; Jiménez-Moreno, E.; Gómez, A. M. ; Corzana, F.; González, C.; Jiménez-Oses, G.; Jiménez-Barbero, J.; Asensio, J. L. *J. Am. Chem. Soc.* **2013**, *135*, 3347–3350.

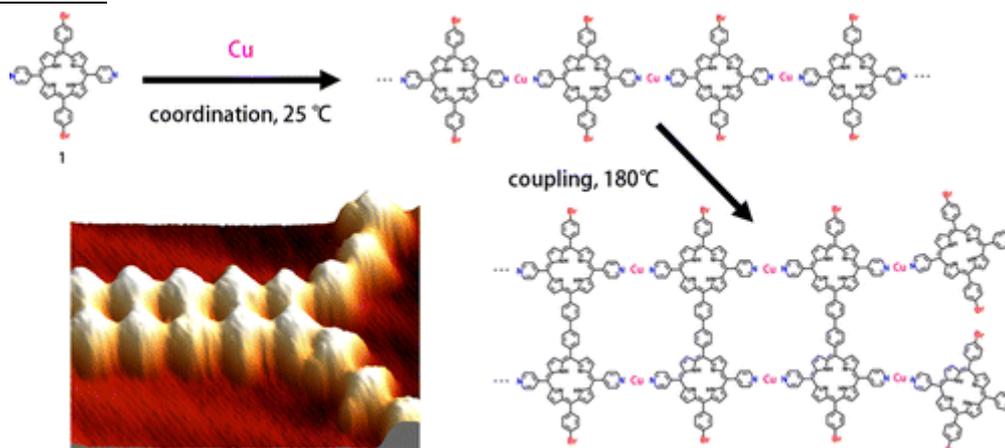
Abstract:



A dynamical combinatorial approach for the study of weak carbohydrate/aromatic interactions is presented. This methodology has been employed to dissect the subtle structure–stability relationships that govern facial selectivity in these supramolecular complexes.

- Steering On-Surface Polymerization with Metal-Directed Template
Lin, T.; Shang, X. S.; Adisojoso, J.; Liu, P. N.; Lin, N. *J. Am. Chem. Soc.* **2013**, *135*, 3576–3582.

Abstract:



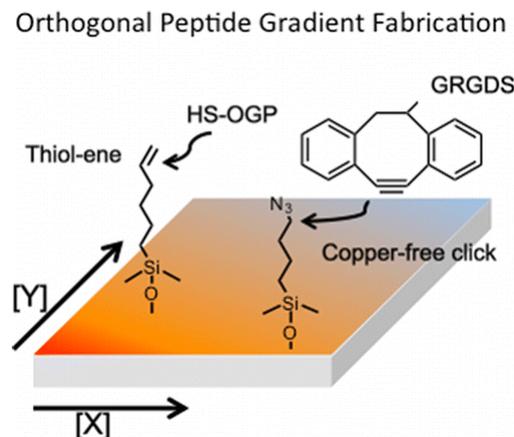
On-surface polymerization represents a novel bottom-up approach for producing macromolecular structures. To date, however, most of the structures formed using this method exhibit a broad size distribution and are disorderly adsorbed on the surface. Here we demonstrate a strategy of using metal-directed template to control the on-surface polymerization process. We chose a bifunctional compound which contains pyridyl and bromine end groups as the precursor. Linear template afforded by pyridyl–Cu–pyridyl coordination effectively promoted Ullmann coupling of the monomers on a Au(111) surface. Taking advantage of efficient topochemical enhancement owing to the conformation flexibility of the Cu–pyridyl bonds, macromolecular porphyrin structures that exhibit a narrow size

distribution were synthesized. We used scanning tunneling microscopy and kinetic Monte Carlo simulation to gain insights into the metal-directed polymerization at the single molecule level. The results reveal that the polymerization process profited from the rich chemistry of Cu which catalyzed the C–C bond formation, controlled the size of the macromolecular products, and organized the macromolecules in a highly ordered manner on the surface.

- Facile Fabrication of “Dual Click” One- and Two-Dimensional Orthogonal Peptide Concentration Gradients

Ma, Y.; Zheng, J.; Amond, E. F.; Stafford, C. M.; Becker, M. L. *Biomacromolecules* **2013**, *14*, 665-671.

Abstract:

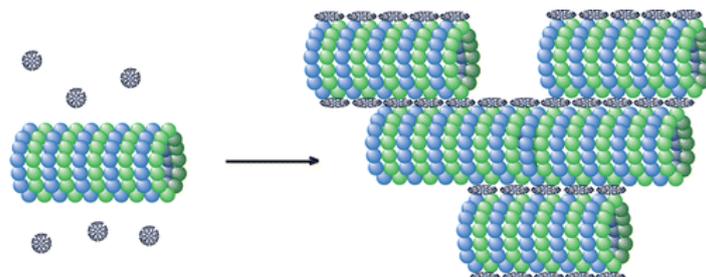


Peptides, proteins, and extracellular matrix act synergistically to influence cellular function at the biotic–synthetic interface. However, identifying the individual and cooperative contributions of the various combinations and concentration regimes is extremely difficult. The confined channel deposition method we describe affords highly tunable orthogonal reactive concentration gradients that greatly expand the dynamic range, spatial control, and chemical versatility of the reactive silanes that can be controllably deposited. Using metal-free “dual click” immobilization chemistries, multiple peptides with a variety of functionality can be immobilized efficiently and reproducibly enabling optimal concentration profiling and the assessment of synergistic interactions.

- Paclitaxel-Conjugated PAMAM Dendrimers Adversely Affect Microtubule Structure through Two Independent Modes of Action

Cline, E. N.; Li, M.-H.; Choi, S. K.; Herbstman, J. F.; Kaul, N.; Meyhöfer, E.; Skiniotis, G.; Baker, J. R.; Larson, R. G.; Walter, N. G. *Biomacromolecules* **2013**, *14*, 654-664.

Abstract:



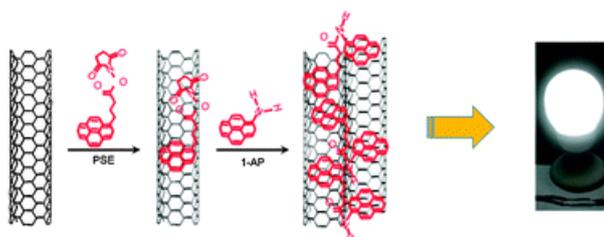
Paclitaxel (Taxol) is an anticancer drug that induces mitotic arrest via microtubule hyperstabilization but causes side effects due to its hydrophobicity and cellular promiscuity. The targeted cytotoxicity of hydrophilic paclitaxel-conjugated polyamidoamine (PAMAM) dendrimers has been demonstrated in

cultured cancer cells. Mechanisms of action responsible for this cytotoxicity are unknown, that is, whether the cytotoxicity is due to paclitaxel stabilization of microtubules, as is whether paclitaxel is released intracellularly from the dendrimer. To determine whether the conjugated paclitaxel can bind microtubules, we used a combination of ensemble and single microtubule imaging techniques in vitro. We demonstrate that these conjugates adversely affect microtubules by (1) promoting the polymerization and stabilization of microtubules in a paclitaxel-dependent manner, and (2) bundling preformed microtubules in a paclitaxel-independent manner, potentially due to protonation of tertiary amines in the dendrimer interior. Our results provide mechanistic insights into the cytotoxicity of paclitaxel-conjugated PAMAM dendrimers and uncover unexpected risks of using such conjugates therapeutically.

- Noncovalently functionalized highly conducting carbon nanotube films with enhanced doping stability via an amide linkage

Chen, I-W. P.; *Chem. Commun.* **2013**, *49*, 2753-2755.

Abstract:

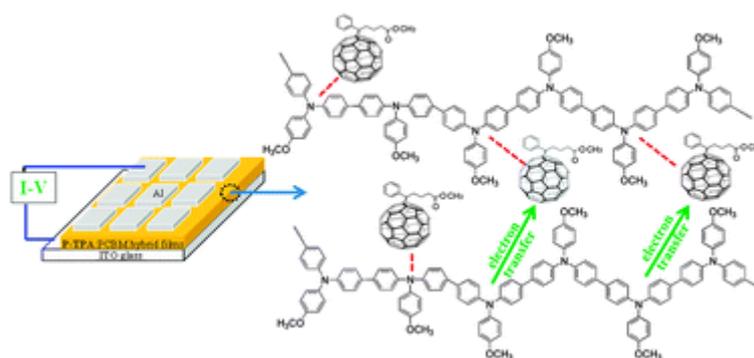


Creating superior electrical properties from macroscopic assembly of carbon nanotubes (CNTs) to replace metal is still an unaccomplished goal. Here we report a noncovalent functionalization method to connect individual CNTs with an electrical conductivity reaching 9150 S cm^{-1} and the mechanical properties can be increased by an order of 1–2.

- Electrically bistable memory devices based on poly(triphenylamine)–PCBM hybrids

Chen, C.-J.; Hu, Y.-C.; Liou, G.-S. *Chem. Commun.* **2013**, *49*, 2804-2806.

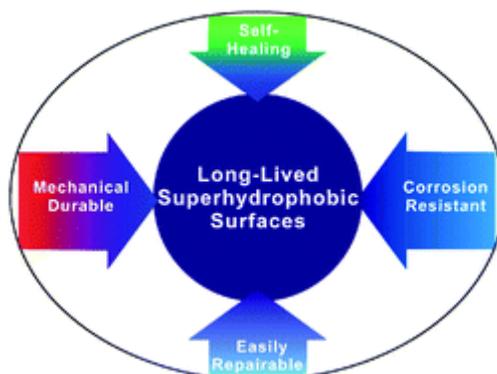
Abstract:



Due to the strong interaction between PCBM and triphenylamine, PCBM could be well distributed into poly-4-methoxytriphenylamine (P-TPA). The resulting hybrid films exhibited DRAM behavior at low PCBM concentrations, while they revealed WORM property at higher, 5 wt% and even up to 10 wt%, PCBM concentrations.

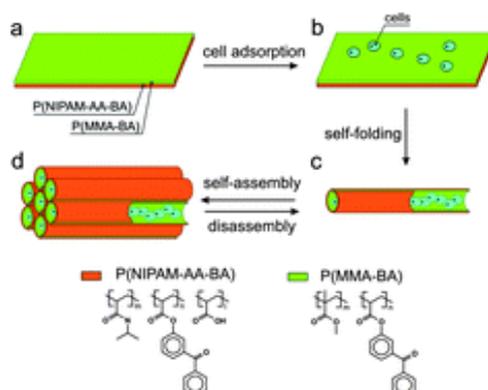
- Long-lived superhydrophobic surfaces

Xue, C.-H.; Ma, J.-Z. *J. Mater. Chem. A* **2013**, *1*, 4146-4161.

Abstract:

Prolonging the lifetime of superhydrophobic surfaces is required so that the materials can be used practically. Thus, great efforts have been made in designing surfaces that maintain micro- and nanoscaled hierarchical structures and low surface-energy property, which are necessary for superhydrophobicity, during use. It was demonstrated that improving surface mechanical strength to increase wear resistance helps maintain hierarchical roughness, retarding the loss of superhydrophobicity. Additionally, designing self-healing materials that can recover their structure and/or properties when damaged has been suggested and demonstrated to sustain the superhydrophobicity of surfaces. This review focuses on recent advances in developing mechanically durable, corrosion-resistant, self-healing, and easily repairable superhydrophobic surfaces, which will enable prolonged lifetime of superhydrophobicity for practical applications in the future.

- Stimuli-responsive hierarchically self-assembled 3D porous polymer-based structures with aligned pores
Zakharchenko, S.; Pureskiy, N.; Stoychev, G.; Waurisch, C.; Hickey, S. G.; Eychmüller, A.; Sommer, J.-U.; Ionov, L. *J. Mater. Chem. B* **2013**, *1*, 1786-1793.

Abstract:

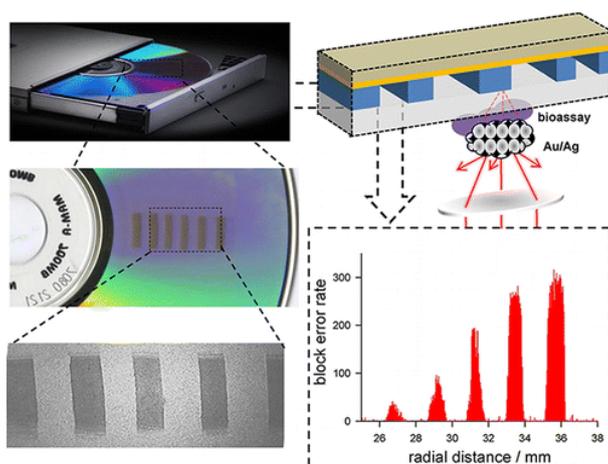
We have developed a novel approach for the fabrication of self-assembled porous materials with uniaxial tubular pores. The approach is based on the use of microtubes formed by stimuli-induced rolling of polymer bilayers consisting of hydrophobic and stimuli-responsive hydrophilic polymers. Different objects, for example yeast cells, can be encapsulated inside the tubes during their rolling. The self-rolled tubes filled with the yeast cells are capable of controlled self-assembly and form a uniaxial tubular homogeneously filled scaffold. Moreover, our approach allows design of porous materials with the pores having different properties.

- Reading Disc-Based Bioassays with Standard Computer Drives

Yu, H.-Z.; Li, Y.; Ou, L. M.-L. *Acc. Chem. Res.* **2013**, *46*, 258–268.

Abstract:

15



Traditional methods of disease diagnosis are both time-consuming and labor-intensive, and many tests require expensive instrumentation and trained professionals, which restricts their use to biomedical laboratories. Because patients can wait several days (even weeks) for the results, the consequences of delayed treatment could be disastrous. Therefore, affordable and simple point-of-care (POC) biosensor devices could fill a diagnostic niche in the clinic or even at home, as personal glucose meters do for diabetics. These devices would allow patients to check their own health conditions and enable physicians to make prompt treatment decisions, which could improve the chances for rapid recovery and cure.

Compact discs (CDs) provide inexpensive substrate materials for the preparation of microarray biochips, and conventional computer drives/disc players can be adapted as precise optical reading devices for signal processing. Researchers can employ the polycarbonate (PC) base of a CD as an alternative substrate to glass slides or silicon wafers for the preparation of microanalytical devices. Using the characteristic optical phenomena occurring on the metal layer of a CD, researchers can develop biosensors based on advanced spectroscopic readout (interferometry or surface plasmon resonance). If researchers integrate microfluidic functions with CD mechanics, they can control fluid transfer through the spinning motion of the disc, leading to “lab-on-a-CD” devices.

Over the last decade, our laboratory has focused on the construction of POC biosensor devices from off-the-shelf CDs or DVDs and standard computer drives. Besides the initial studies of the suitability of CDs for surface and materials chemistry research (fabrication of self-assembled monolayers and oxide nanostructures), we have demonstrated that an ordinary optical drive, without modification of either the hardware or the software driver, can function as the signal transducing element for reading disc-based bioassays quantitatively.

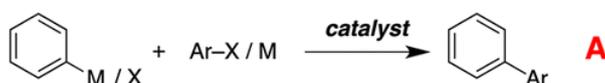
In this Account, we first provide a brief introduction to CD-related materials chemistry and microfluidics research. Then we describe the mild chemistry developed in our laboratory for the preparation of computer-readable biomolecular screening assays: photochemical activation of the polycarbonate (PC) disc surface and immobilization and delivery of probe and target biomolecules. We thoroughly discuss the analysis of the molecular recognition events: researchers can “read” these devices quantitatively with an unmodified optical drive of any personal computer. Finally, and critically, we illustrate our digitized molecular diagnosis approach with three trial systems: DNA hybridization, antibody–antigen binding, and ultrasensitive lead detection with a DNAzyme assay. These examples demonstrate the broad potential of this new analytical/diagnostic tool for medical screening, on-site food/water safety testing, and remote environmental monitoring.

- Direct Functionalization Processes: A Journey from Palladium to Copper to Iron to Nickel to Metal-Free Coupling Reactions

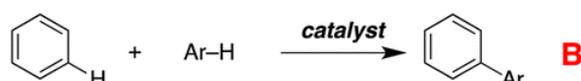
Mousseau, J. J.; Charette, A. B. *Acc. Chem. Res.* **2013**, *46*, 339–349.

Abstract:

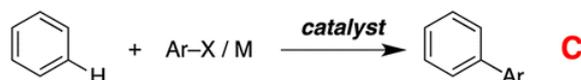
Traditional Cross-Coupling



Oxidative Coupling of C–H Bonds



Direct Arylation



The possibility of finding novel disconnections for the efficient synthesis of organic molecules has driven the interest in developing technologies to directly functionalize C–H bonds. The ubiquity of these bonds makes such transformations attractive, while also posing several challenges. The first, and perhaps most important, is the selective functionalization of one C–H bond over another. Another key problem is inducing reactivity at sites that have been historically unreactive and difficult to access without prior inefficient prefunctionalization.

Although remarkable advances have been made over the past decade toward solving these and other problems, several difficult tasks remain as researchers attempt to bring C–H functionalization reactions into common use. The functionalization of sp^3 centers continues to be challenging relative to their sp and sp^2 counterparts. Directing groups are often needed to increase the effective concentration of the catalyst at the targeted reaction site, forming thermodynamically stable coordination complexes. As such, the development of removable or convertible directing groups is desirable. Finally, the replacement of expensive rare earth reagents with less expensive and more sustainable catalysts or abandoning the use of catalysts entirely is essential for future practicality.

This Account describes our efforts toward solving some of these quandaries. We began our work in this area with the direct arylation of *N*-iminopyridinium ylides as a universal means to derivatize the germane six-membered heterocycle. We found that the Lewis basic benzoyl group of the pyridinium ylide could direct a palladium catalyst toward insertion at the 2-position of the pyridinium ring, forming a thermodynamically stable six-membered metallocycle. Subsequently we discovered the arylation of the benzylic site of 2-picolonium ylides. The same *N*-benzoyl group could direct a number of inexpensive copper salts to the 2-position of the pyridinium ylide, which led to the first description of a direct copper-catalyzed alkenylation onto an electron-deficient arene. This particular directing group offers two advantages: (1) it can be easily appended and removed to reveal the desired pyridine target, and (2) it can be incorporated in a cascade process in the preparation of pharmacologically relevant 2-pyrazolo[1,5-*a*]pyridines.

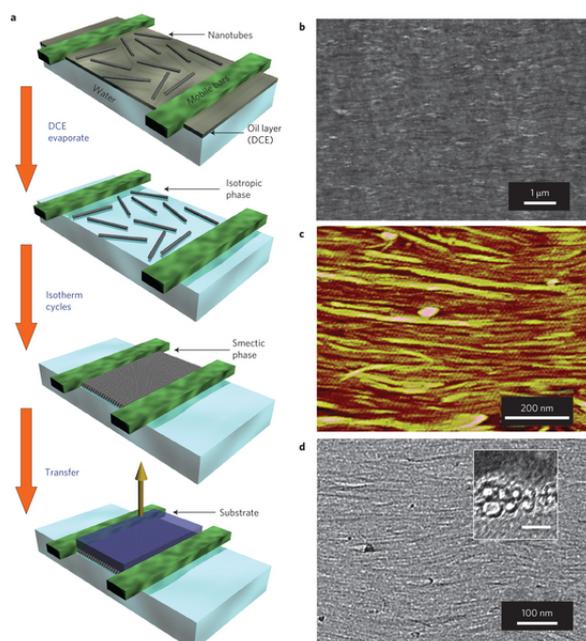
This work has solved some of the challenges in the direct arylation of nonheterocyclic arenes, including reversing the reactivity often observed with such transformations. Readily convertible directing groups were applied to facilitate the transformation. We also demonstrated that iron can

promote intermolecular arylations effectively and that the omission of any metal still permits intramolecular arylation reactions. Lastly, we recently discovered a nickel-catalyzed intramolecular arylation of sp^3 C–H bonds. Our mechanistic investigations of these processes have elucidated radical pathways, opening new avenues in future direct C–H functionalization reactions.

- Arrays of single-walled carbon nanotubes with full surface coverage for high-performance electronics

Cao, Q.; Han, S.; Tulevski, G.S.; Zhu, Y.; Lu, D.D.; Haensch, W. *Nature Nano.* **2013**, *8*, 180–186.

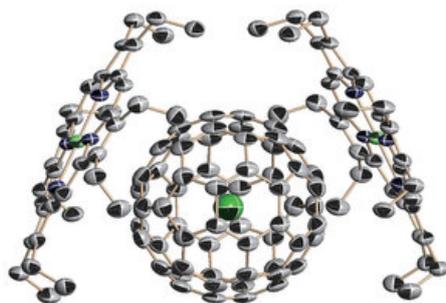
Abstract:



Single-walled carbon nanotubes have exceptional electronic properties and have been proposed as a replacement for silicon in applications such as low-cost thin-film transistors and high-performance logic devices¹. However, practical devices will require dense, aligned arrays of electronically pure nanotubes to optimize performance, maximize device packing density and provide sufficient drive current (or power output) for each transistor². Here, we show that aligned arrays of semiconducting carbon nanotubes can be assembled using the Langmuir–Schaefer method. The arrays have a semiconducting nanotube purity of 99% and can fully cover a surface with a nanotube density of more than 500 tubes/ μm . The nanotube pitch is self-limited by the diameter of the nanotube plus the van der Waals separation, and the intrinsic mobility of the nanotubes is preserved after array assembly. Transistors fabricated using this approach exhibit significant device performance characteristics with a drive current density of more than $120 \mu\text{A} \mu\text{m}^{-1}$, transconductance greater than $40 \mu\text{S} \mu\text{m}^{-1}$ and on/off ratios of $\sim 1 \times 10^3$.

- X-ray observation of a helium atom and placing a nitrogen atom inside He@C60 and He@C70
Morinaka, Y.; Sato, S.; Wakamiya, A.; Nikawa, H.; Mizorogi, N.; Tanabe, F.; Murata, M.; Komatsu, K.; Furukawa, K.; Kato, T.; Nagase, S.; Akasaka, T.; Murata, Y. *Nat Commun.* **2013**, *4*, 1554.

Abstract:

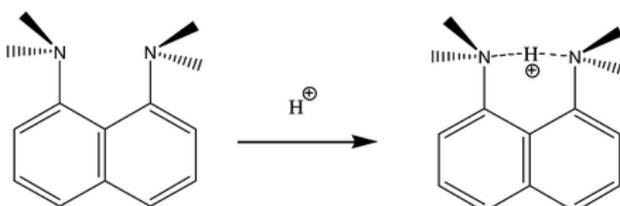


Single crystal X-ray analysis has been used as a powerful method to determine the structure of molecules. However, crystallographic data containing helium has not been reported, owing to the difficulty in embedding helium into crystalline materials. Here we report the X-ray diffraction study of He@C₆₀ and the clear observation of a single helium atom inside C₆₀. In addition, the close packing of a helium atom and a nitrogen atom inside fullerenes is realized using two stepwise insertion techniques, that is, molecular surgery to synthesize the fullerenes encapsulating a helium atom, followed by nitrogen radio-frequency plasma methods to generate the fullerenes encapsulating both helium and nitrogen atoms. Electron spin resonance analysis reveals that the encapsulated helium atom has a small but detectable influence on the electronic properties of the highly reactive nitrogen atom coexisting inside the fullerene, suggesting the potential usage of helium for controlling electronic properties of reactive species.

- Synthesis of an extra-large molecular sieve using proton sponges as organic structure-directing agents

Martínez-Franco, R.; Moliner, M.; Yun, Y.; Sun, J.; Wan, W.; Zou, X.; Corma, A. *Proc. Nat. Acad. Sci. USA* **2013**, *110*, 3749-3754.

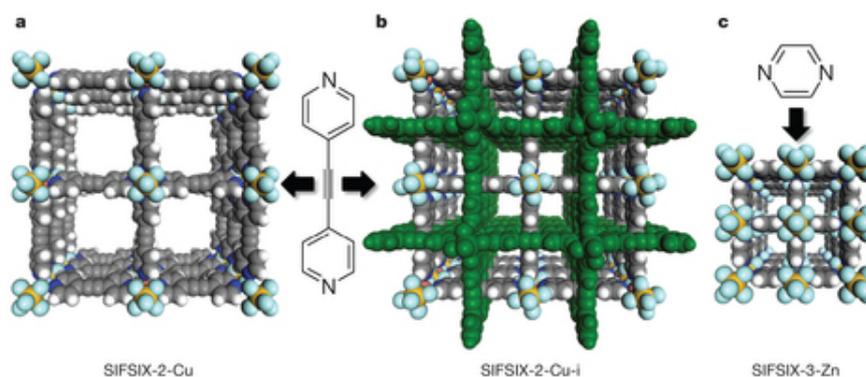
Abstract:



The synthesis of crystalline microporous materials containing large pores is in high demand by industry, especially for the use of these materials as catalysts in chemical processes involving bulky molecules. An extra-large-pore silicoaluminophosphate with 16-ring openings, ITQ-51, has been synthesized by the use of bulky aromatic proton sponges as organic structure-directing agents. Proton sponges show exceptional properties for directing extra-large zeolites because of their unusually high basicity combined with their large size and rigidity. This extra-large-pore material is stable after calcination, being one of the very few examples of hydrothermally stable molecular sieves containing extra-large pores. The structure of ITQ-51 was solved from submicrometer-sized crystals using the rotation electron diffraction method. Finally, several hypothetical zeolites related to ITQ-51 have been proposed.

- Porous materials with optimal adsorption thermodynamics and kinetics for CO₂ separation
Patrick Nugent, P.; Belmabkhout, Y.; Burd, S. D.; Cairns, A. J.; Luebke, R.; Forrest, K.; Pham, T.; Ma, S.; Space, B.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. *Nature* **2013**, *495*, 80-84.

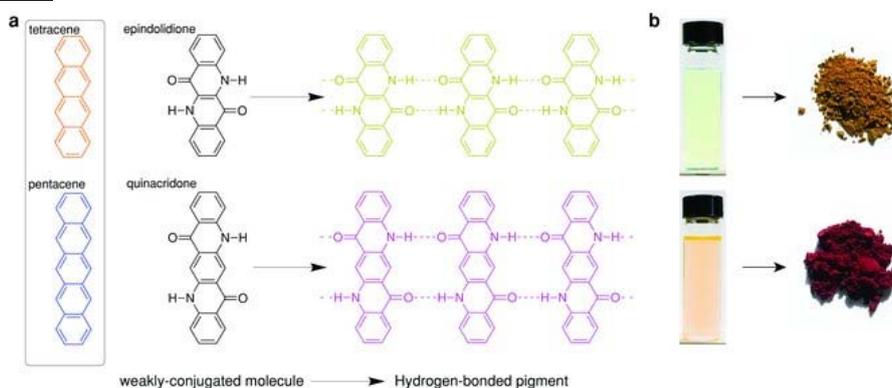
Abstract:



The energy costs associated with the separation and purification of industrial commodities, such as gases, fine chemicals and fresh water, currently represent around 15 per cent of global energy production, and the demand for such commodities is projected to triple by 2050. The challenge of developing effective separation and purification technologies that have much smaller energy footprints is greater for carbon dioxide (CO₂) than for other gases; in addition to its involvement in climate change, CO₂ is an impurity in natural gas, biogas (natural gas produced from biomass), syngas (CO/H₂, the main source of hydrogen in refineries) and many other gas streams. In the context of porous crystalline materials that can exploit both equilibrium and kinetic selectivity, size selectivity and targeted molecular recognition are attractive characteristics for CO₂ separation and capture, as exemplified by zeolites 5A and 13X, as well as metal–organic materials (MOMs). Here we report that a crystal engineering or reticular chemistry strategy that controls pore functionality and size in a series of MOMs with coordinately saturated metal centres and periodically arrayed hexafluorosilicate (SiF₆²⁻) anions enables a ‘sweet spot’ of kinetics and thermodynamics that offers high volumetric uptake at low CO₂ partial pressure (less than 0.15 bar). Most importantly, such MOMs offer an unprecedented CO₂ sorption selectivity over N₂, H₂ and CH₄, even in the presence of moisture. These MOMs are therefore relevant to CO₂ separation in the context of post-combustion (flue gas, CO₂/N₂), pre-combustion (shifted synthesis gas stream, CO₂/H₂) and natural gas upgrading (natural gas clean-up, CO₂/CH₄).

- Hydrogen-Bonded Semiconducting Pigments for Air-Stable Field-Effect Transistors
 Głowacki, E. D.; Irimia-Vladu, M.; Kaltenbrunner, M.; Gsiorowski, J.; White, M. S.; Monkowius, U.; Romanazzi, G.; Suranna, G. P.; Mastroianni, P.; Sekitani, T.; Bauer, S.; Someya, T.; Torsi, L.; Sariciftci, N. S. *Adv. Mater.* **2013**, *25*, 1563–1569.

Abstract:

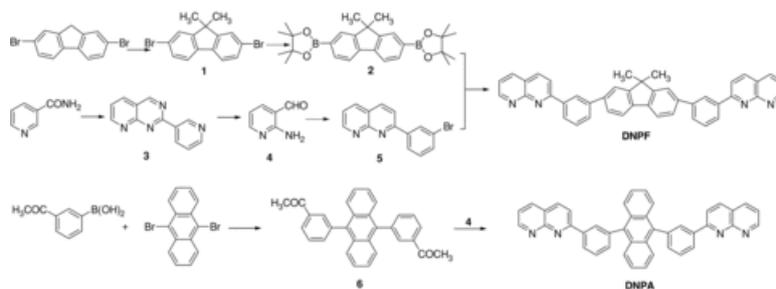


Extensive intramolecular π -conjugation is considered to be requisite in the design of organic semiconductors. Here, two inkjet pigments, epindolidione and quinacridone, that break this design

rule are explored. These molecules afford intermolecular π -stacking reinforced by hydrogen-bonding bridges. Air-stable organic field effect transistors are reported that support mobilities up to $1.5 \text{ cm}^2/\text{Vs}$ with T_{80} lifetimes comparable with the most stable reported organic semiconducting materials.

- Highly Efficient Electron-Transporting/Injecting and Thermally Stable Naphthyridines for Organic Electrophosphorescent Devices
Xiao, L.; Xing, X.; Chen, Z.; Qu, B.; Lan, H.; Gong, Q.; Kido, J. *Adv. Funct. Mater.* **2013**, *23*, 1323–1330.

Abstract:



A series of 1,8-naphthyridine derivatives is synthesized and their electron-transporting/injecting (ET/EI) properties are investigated via a multilayered electrophosphorescent organic light-emitting device (OLED) using *fac*-tris(2-phenylpyridine)iridium [$\text{Ir}(\text{ppy})_3$] as a green phosphorescent emitter doped into a 4,4'-*N,N'*-dicarbazolebiphenyl (CBP) host with 4,4'-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (α -NPD) as the hole-transporting layer, and poly(arylene ether sulfone) containing tetraphenylbenzidine (TPDPES) doped with tris(4-bromophenyl)ammonium hexachloroantimonate (TBPAAH) as the hole-injecting layer. The turn-on voltage of the device is 2.5 V using 2,7-bis[3-(2-phenyl)-1,8-naphthyridinyl]-9,9-dimethylfluorene (DNPF), lower than that of 3.0 V for the device using a conventional ET material. The maximum current efficiency (CE) and power efficiency (PE) of the DNPF device are much higher than those of a conventional device. With the aid of a hole-blocking (HB) and exciton-blocking layer of bathocuproine (BCP), 13.2–13.7% of the maximum external quantum efficiency (EQE) and a maximum PE of $50.2\text{--}54.5 \text{ lm W}^{-1}$ are obtained using the naphthyridine derivatives; these values are comparable with or even higher than the 13.6% for conventional ET material. The naphthyridine derivatives show high thermal stabilities, glass-transition temperatures much higher than that of aluminum(III) bis(2-methyl-8-quinolino)-4-phenylphenolate (BALq), and decomposition temperatures of 510–518 °C, comparable to or even higher than those of Alq₃.