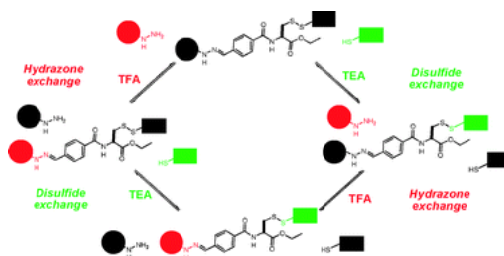


- Covalent double level dynamic combinatorial libraries: selectively addressable exchange processes

1

Orrillo, A. G.; Escalante, A. M.; Furlan, R. L. E. *Chem. Commun.* **2008**, 5298–5300.

Abstract :

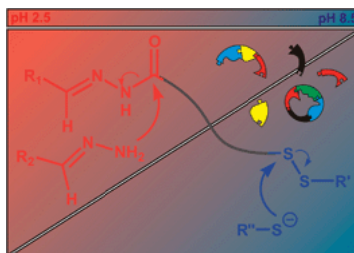


Hydrazones and disulfides have been combined in one dynamic system: hydrazones were exchanged by acid catalysis in the presence of disulfide and a thiol group without interference; neutralization of the reaction medium turns off the exchange of hydrazones and, at the same time, activates thiolate–disulfide exchange.

- Orthogonal or simultaneous use of disulfide and hydrazone exchange in dynamic covalent chemistry in aqueous solution

Rodriguez-Docampo, Z.; Otto, S. *Chem. Commun.* **2008**, 5301–5303.

Abstract :

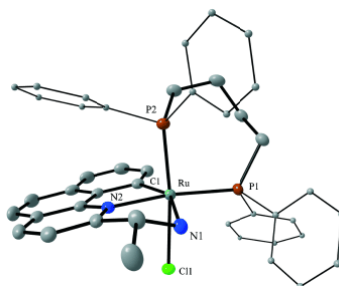


Hydrazone and disulfide exchange have been combined in a single system, but can be addressed independently: by adjusting the pH of the solution from acidic to mildly basic it is possible to switch from exclusively hydrazone exchange to exclusively disulfide exchange, while at intermediate pH both reactions occur simultaneously.

- New Benzo[*h*]quinoline-Based Ligands and their Pincer Ru and Os Complexes for Efficient Catalytic Transfer Hydrogenation of Carbonyl Compounds

Walter Baratta, W.; Ballico, M.; Baldino, S.; Chelucci, G.; Herdtweck, E.; Siega, K.; Magnolia, S.; Rigo, P. *Chem. Eur. J.* **2008**, *14*, 9148–9160.

Abstract :



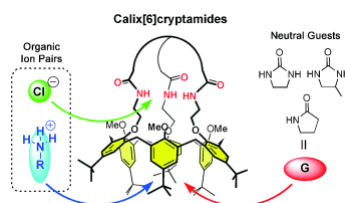
New benzo[*h*]quinoline ligands (HCN<sup>*r*</sup>N) containing a CHRNH<sub>2</sub> (R=H (**a**), Me (**b**), *t*Bu (**c**)) function in the 2-position were prepared starting from benzo[*h*]quinoline *N*-oxide (in the case of ligand **a**) and 2-chlorobenzo[*h*]quinoline (for ligands **b** and **c**). These compounds were used to prepare ruthenium

and osmium complexes, which are excellent catalysts for the transfer hydrogenation (TH) of ketones. The reaction of **a** with  $[\text{RuCl}_2(\text{PPh}_3)_3]$  in 2-propanol at reflux afforded the terdentate CN<sup>r</sup>N complex  $[\text{RuCl}(\text{CN}^r\text{N})(\text{PPh}_3)_2]$  (**1**), whereas the complexes  $[\text{RuCl}(\text{CN}^r\text{N})(\text{dppb})]$  (**2-4**;  $\text{dppb}=\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$ ) were obtained from  $[\text{RuCl}_2(\text{PPh}_3)(\text{dppb})]$  with **a-c**, respectively. Employment of (*R,S*)-Josiphos, (*S,R*)-Josiphos\*, (*S,S*)-Skewphos, and (*S*)-MeO-Biphep in combination with  $[\text{RuCl}_2(\text{PPh}_3)_3]$  and ligand **a** gave the chiral derivatives  $[\text{RuCl}(\text{CN}^r\text{N})(\text{PP})]$  (**5-8**). The osmium complex  $[\text{OsCl}(\text{CN}^r\text{N})(\text{dppb})]$  (**12**) was prepared by treatment of  $[\text{OsCl}_2(\text{PPh}_3)_3]$  with dppb and ligand **a**. Reaction of the chloride **2** and **12** with NaOiPr in 2-propanol/toluene afforded the hydride complexes  $[\text{MH}(\text{CN}^r\text{N})(\text{dppb})]$  (M=Ru **10**, Os **14**), through elimination of acetone from  $[\text{M}(\text{OiPr})(\text{CN}^r\text{N})(\text{dppb})]$  (M=Ru **9**, Os **13**). The species **9** and **13** easily reacted with 4,4'-difluorobenzophenone, via **10** and **14**, respectively, affording the corresponding isolable alkoxides  $[\text{M}(\text{OR})(\text{CN}^r\text{N})(\text{dppb})]$  (M=Ru **11**, Os **15**). The complexes  $[\text{MX}(\text{CN}^r\text{N})(\text{P}_2)]$  (**1-15**) (M=Ru, Os; X=Cl, H, OR; P=PPh<sub>3</sub> and P<sub>2</sub>=diphosphane) are efficient catalysts for the TH of carbonyl compounds with 2-propanol in the presence of NaOiPr (2 mol %). Turnover frequency (TOF) values up to  $1.8 \times 10^6 \text{ h}^{-1}$  have been achieved using 0.02-0.001 mol % of catalyst. Much the same activity has been observed for the Ru —Cl, —H, —OR, and the Os —Cl derivatives, whereas the Os —H and Os —OR derivatives display significantly lower activity on account of their high oxygen sensitivity. The chiral Ru complexes **5-8** catalyze the asymmetric TH of methyl-aryl ketones with TOF  $\approx 10^5 \text{ h}^{-1}$  at 60 °C, up to 97 % enantiomeric excess (*ee*) and remarkably high productivity (0.005 mol % catalyst loading). High catalytic activity (TOF up to  $2.2 \times 10^5 \text{ h}^{-1}$ ) and enantioselectivity (up to 98 % *ee*) have also been achieved with the in-situ-generated catalysts prepared from  $[\text{MCl}_2(\text{PPh}_3)_3]$ , (*S,R*)-Josiphos or (*S,R*)-Josiphos\*, and the benzo[*h*]quinoline ligands **a-c**.

- Synthesis and Study of Calix[6]cryptamides: A New Class of Heteroditopic Receptors that Display Versatile Host-Guest Properties Toward Neutral Species and Organic Associated Ion-Pair Salts

Le Gac, S.; Jabin, I. *Chem. Eur. J.* **2008**, *14*, 548–557.

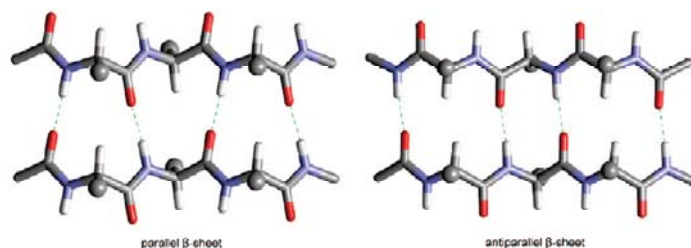
Abstract :



The synthesis of a new family of molecular receptors, namely the calix[6]cryptamides, was achieved through an original [1+1] macrocyclization step that consists of a peptide-coupling reaction between tripodal triscarboxylic acids and a calix[6]trisamine subunit. Several C<sub>3v</sub>- or C<sub>3h</sub>-symmetrical calix[6]arene-based compounds capped by a trisamido cryptand unit on the narrow rim have been obtained, with the more flexible partners leading to the best yields. These calix[6]cryptamides exhibit two favorably positioned binding sites for the complexation of organic-associated ion pairs in close proximity: a well-defined calix[6]arene cavity suitable for the inclusion of ammonium ions and a cryptamide unit for the coordination of anions. We demonstrate one example, chiral calix[6]cryptamide **12**, that constitutes a heteroditopic receptor capable of cooperatively binding both a primary ammonium ion and its chloride counterion, thanks to a combination of polarization and induced-fit effects. In addition, the hydrophobic calixarene cavity of **12** can strongly bind neutral guests through hydrogen bonding and is capable of discriminating between different enantiomers. All these versatile host-guest properties differ greatly from those observed in the parent calix[6]azacryptands.

- Exploring  $\beta$ -Sheet Structure and Interactions with Chemical Model Systems  
Nowick, J. S. *Acc. Chem. Res.* **2008**, *41*, 1319–1330.

Abstract :

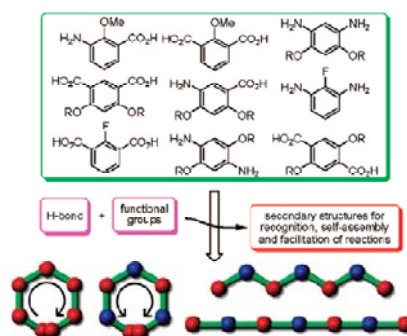


*What I cannot create, I do not understand.—Richard P. Feynman*

$\beta$ -Sheets consist of extended polypeptide strands ( $\beta$ -strands) connected by a network of hydrogen bonds and occur widely in proteins. Although the importance of  $\beta$ -sheets in the folded structures of proteins has long been recognized, there is a growing recognition of the importance of intermolecular interactions among  $\beta$ -sheets. Intermolecular interactions between the hydrogen-bonding edges of  $\beta$ -sheets constitute a fundamental form of biomolecular recognition (like DNA base pairing) and are involved protein quaternary structure, protein–protein interactions, and peptide and protein aggregation. The importance of  $\beta$ -sheet interactions in biological processes makes them potential targets for intervention in diseases such as AIDS, cancer, and Alzheimer’s disease. This Account describes my research group’s use of chemical model systems to study the structure and interactions of  $\beta$ -sheets. Chemical model systems provide an excellent vehicle with which to explore  $\beta$ -sheets, because they are smaller, simpler, and easier to manipulate than proteins. Synthetic chemical models also provide the opportunity to control or modulate natural systems or to develop other useful applications and may eventually lead to new drugs with which to treat diseases. In our “artificial  $\beta$ -sheets”, molecular template and turn units are combined with peptides to mimic the structures of parallel and antiparallel  $\beta$ -sheets. The templates and turn units form folded, hydrogen-bonded structures with the peptide groups and help prevent the formation of complex, ill-defined aggregates. Templates that duplicate the hydrogen-bonding pattern of one edge of a peptide  $\beta$ -strand while blocking the other edge have proven particularly valuable in preventing aggregate formation and in promoting the formation of simple monomeric and dimeric structures. Artificial  $\beta$ -sheets that present exposed hydrogen-bonding edges can form well-defined hydrogen-bonded dimers. Dimerization occurs readily in chloroform solutions but requires additional hydrophobic interactions to occur in aqueous solution. Interactions among the side chains, as well as hydrogen bonding among the main chains, are important in dimer formation. NMR studies of artificial  $\beta$ -sheets have elucidated the importance of hydrogen-bonding complementarity, size complementarity, and chiral complementarity in these interactions. These pairing preferences demonstrate sequence selectivity in the molecular recognition between  $\beta$ -sheets. These studies help illustrate the importance of *intermolecular* edge-to-edge interactions between  $\beta$ -sheets in peptides and proteins. Ultimately, these model systems may lead to new ways of controlling  $\beta$ -sheet interactions and treating diseases in which they are involved.

- Peptide Mimics by Linear Arylamides: A Structural and Functional Diversity Test  
Li, Z.-T.; Hou, J.-L.; Li, C. *Acc. Chem. Res.* **2008**, *41*, 1343–1353.

Abstract :

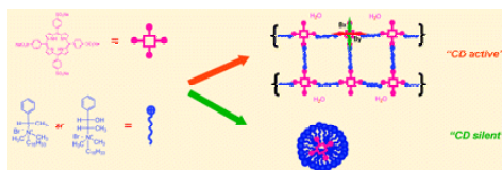


Hydrogen-bonded oligoamide foldamers represent a large family of peptide mimics. Pioneered by Gellman and Seebach ( Appella, , et al. *J. Am. Chem. Soc.* **1996**, *118*, 13071–13072; Seebach, , et al. *Helv. Chim. Acta* **1996**, *79*, 913–941), aliphatic amino acid-based mimic structures have been extensively studied. Results of these studies have found many useful applications in areas including chemical biology and drug design. This Account describes our efforts in creating arylamide-based foldamers whose compact conformations are stabilized by hydrogen bonding. The aim of our study was to test whether this class of mimic structures is sufficiently rigid to lead to new interesting functions. It was envisioned that, if our approach was workable, it might be developed into a new family of useful soft frameworks for studies toward molecular recognition, self-assembly, and materials science. Three classes of mimic structures, that is, folded or helical, zigzag, and straight oligomers, have been constructed by simply changing the positions of the substituents at the benzene rings in the backbones. Both amide and hydrazide units have been employed to construct the frameworks. In most cases, O···H–N hydrogen bonding was chosen to stabilize the compact conformations. Notably, for the first time the F···H–N hydrogen-bonding pattern has been used to tune the size of the cavity. To test their usefulness, these frameworks have been extensively modified and functionalized. <sup>1</sup>H NMR, UV–vis, fluorescence, circular dichroism, and X-ray diffraction techniques have all been employed to establish the compact structures and their interactions with guest molecules. The properties or functions of the mimic structures have been studied in seven aspects. (1) Acyclic molecular receptors: The amide foldamers can bind amine cations, while the hydrazide foldamers can complex saccharides. (2) Acceleration of anisole hydrolysis: Several folded oligomers are able to bind alkali metal cations and consequently promote the hydrolysis of the nitro-substituted anisole by alkali hydroxides. (3) Facilitation of macrocyclization: The straight and zigzag backbones can be readily functionalized, from which two classes of macrocycles have been prepared. (4) Homoduplex assembly: Zigzag oligomers that are appended with amide units at one side can form stable homoduplexes through the cooperative self-binding of the amide units. (5) Assembly of molecular tweezers: Discrete binding moieties are introduced at the ends of the oligomers, which can bind structurally matched guests. (6) Assembly of nano networks: F···H–N hydrogen-bonded foldamers can stack with fullerenes; thus a mixture of fullerenes with a trifoldamer generates honeycomb-styled nanoarchitectures. (7) Assembly of dynamic [2]catenanes: A preorganized porphyrin tweezer has been synthesized, from which dynamic three-component [2]catenanes have been assembled in high yields. Our results demonstrate that hydrogen-bonding-driven arylamide oligomers are a class of structurally unique mimic structures. The folded oligomers themselves can be used as synthetic receptors for binding different guest molecules, while incorporation of different segments into one system can produce many desired shapes. In addition, all of the rigid frameworks can be readily functionalized at specific sites. We believe that our results have helped to open the door for some new chemistry in molecular recognition, self-assembly, and other related areas.

- Role of the Hydrophobic Effect in the Transfer of Chirality from Molecules to Complex Systems: From Chiral Surfactants to Porphyrin/Surfactant Aggregates  
El-Hachemi, Z.; Mancini, G.; Ribó, J. M.; Sorrenti, A. *J. Am. Chem. Soc.* **2008**, *130*, 15176–15184.

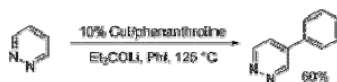
Abstract :

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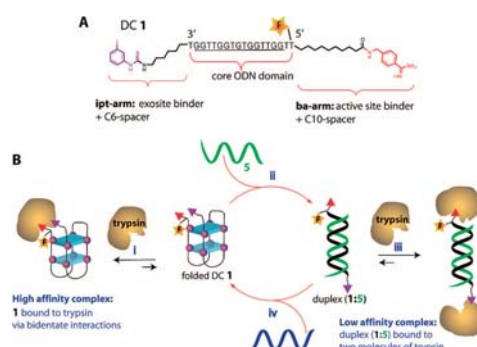
The interaction between the achiral sulfonated porphyrin 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin,  $H_2TPPS_4^{4-}$ , and two chiral cationic surfactants has been studied by optical absorption, fluorescence, and circular dichroism (CD) spectroscopies. At surfactant concentrations above the critical micellar concentration (cmc) the porphyrin is included in the micellar aggregates, but it is CD silent. Below the cmc at a definite porphyrin/surfactant stoichiometry the formation of heteroaggregates with transfer of chirality to the porphyrin chromophore occurs. The preferred surfactant/porphyrin stoichiometry is 3:1, which suggests a structure driven by electrostatic and hydrophobic interactions between porphyrin and surfactant and dipolar and ionic interactions with the water solution. At surfactant concentrations above the cmc, depending on the protocol of preparation of the samples, the formation of the two kinds of aggregates can be observed, reversible for the simple surfactant micelles incorporating the porphyrin, but irreversible for the heteroaggregates.

- A General Method for Copper-Catalyzed Arylation of Arene C-H Bonds  
Do, H.-Q.; Kashif Khan, R. M.; Daugulis, O. *J. Am. Chem. Soc.* **2008**, *130*, 15185–15192.

Abstract :

A general method for copper-catalyzed arylation of  $sp^2$  C-H bonds with  $pK_a$ 's below 35 has been developed. The method employs aryl halide as the coupling partner, lithium alkoxide or  $K_3PO_4$  base, and DMF, DMPU, or mixed DMF/xylenes solvent. A variety of electron-rich and electron-poor heterocycles such as azoles, caffeine, thiophenes, benzofuran, pyridine oxides, pyridazine, and pyrimidine can be arylated. Furthermore, electron-poor arenes possessing at least two electron-withdrawing groups on a benzene ring can also be arylated. Two arylcopper-phenanthroline complex intermediates were independently synthesized.

- DNA-Small Molecule Chimera with Responsive Protein-Binding Affinity  
Harris, D. C.; Chu, X.; Jayawickramarajah, J. *J. Am. Chem. Soc.* **2008**, *130*, 14950–14951.

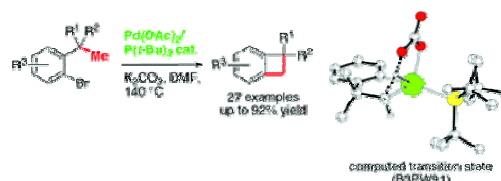
Abstract :

In this communication, we disclose a generalizable strategy for developing agents with regulable protein-binding ability. In particular, a responsive DNA-small molecule chimera (DC) 1 consisting of two synthetic protein-binding arms and a core oligonucleotide (ODN) domain is discussed. DC 1 can

be cycled from a bidentate intramolecular quadruplex form to a monodentate duplex structure, via addition of external ODN stimuli. Importantly, these distinct secondary structures of **1** lead to significantly different protein-binding abilities, with the bidentate conformation showing a 20-fold enhancement (with a 0.8  $\mu\text{M}$  dissociation constant,  $K_d$ ) in trypsin-binding potency.

- Synthesis of Benzocyclobutenes by Palladium-Catalyzed C–H Activation of Methyl Groups: Method and Mechanistic Study  
Chaumontet, M.; Piccardi, R.; Audic, N.; Hitce, J.; Peglion, J.-L.; Clot, E.; Baudoin, O. *J. Am. Chem. Soc.* **2008**, *130*, 15157–15166.

Abstract :



An efficient catalytic system has been developed for the synthesis of benzocyclobutenes by C–H activation of methyl groups. The optimal conditions employed a combination of  $\text{Pd}(\text{OAc})_2$  and  $\text{P}^t\text{Bu}_3$  as catalyst,  $\text{K}_2\text{CO}_3$  as the base, and DMF as solvent. A variety of substituted BCB were obtained under these conditions with yields in the 44–92% range, including molecules that are hardly accessible by other methods. The reaction was found limited to substrates bearing a quaternary benzylic carbon, but benzocyclobutenes bearing a tertiary benzylic carbon could be obtained indirectly from diesters by decarboxylation. Reaction substrates bearing a small substituent *para* to bromine gave an unexpected regioisomer that likely arose from a 1,4-palladium migration process. The formation of this “abnormal” regioisomer could be suppressed by introducing a larger substituent *para* to bromine. DFT(B3PW91) calculations on the reaction of 2-bromo-*tert*-butylbenzene with  $\text{Pd}(\text{P}^t\text{Bu}_3)$  with different bases (acetate, bicarbonate, carbonate) showed the critical influence of the coordination mode of the base to induce both an easy C–H activation and to allow for a pathway for 1,4-palladium migration. Carbonate is shown to be more efficient than the two other bases because it can abstract the proton easily and at the same time maintain  $\kappa^1$ -coordination without extensive electronic reorganization.

- Structural selection of graphene supramolecular assembly oriented by molecular conformation and alkyl chain  
Chen, Q.; Chen, T.; Pan, G.-B.; Yan, H.-J.; Song, W.-G.; Wan, L.-H.; Li, Z.-T.; Wang, Z.-H.; Shang, B.; Yuan, L.-F.; Yang, J.-L. *P. N. A. S.* **2008**, *105*, 16849–16854.

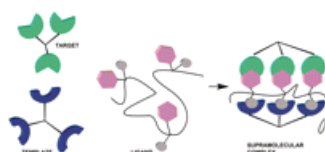
Abstract :

Graphene molecules, hexafluorotribenzo[*a,g,m*]coronene with *n*-carbon alkyl chains (FTBC-C<sub>*n*</sub>, *n* = 4, 6, 8, 12) and Janus-type “double-concave” conformation, are used to fabricate self-assembly on highly oriented pyrolytic graphite surface. The structural dependence of the self-assemblies with molecular conformation and alkyl chain is investigated by scanning tunneling microscopy and density functional theory calculation. An interesting reverse face “up–down” way is observed in FTBC-C<sub>4</sub> assembly due to the existence of hydrogen bonds. With the increase of the alkyl chain length and consequently stronger van der Waals interaction, the molecules no longer take alternating “up–down” orientation in their self-assembly and organize into various adlayers with lamellar, hexagonal

honeycomb, and pseudohoneycomb structures based on the balance between intermolecular and molecule-substrate interactions. The results demonstrate that the featured “double-concave” molecules are available block for designing graphene nanopattern. From the results of scanning tunneling spectroscopy measurement, it is found that the electronic property of the featured graphene molecules is preserved when they are adsorbed on solid surface.

- In vivo supramolecular templating enhances the activity of multivalent ligands: A potential therapeutic against the *Escherichia coli* O157 AB<sub>5</sub> toxins  
Kitov, P. I.; Mulvey, G. L.; Griener, T. P.; Lipinski, T.; Solomon, D.; Paszkiewicz, E.; Jacobson, J. M.; Sadowska, J. M.; Suzuki, M.; Yamamura, K.-I.; Armstrong, G. D.; Bundle, D. R. *P. N. A. S.* **2008**, *105*, 16849–16854.

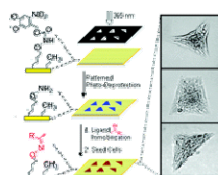
Abstract :



We demonstrate that interactions between multimeric receptors and multivalent ligands are dramatically enhanced by recruiting a complementary templating receptor such as an endogenous multimeric protein but only when individual ligands are attached to a polymer as preorganized, covalent, heterobifunctional pairs. This effect cannot be replicated by a multivalent ligand if the same recognition elements are independently arrayed on the scaffold. Application of this principle offers an approach to create high-avidity inhibitors for multimeric receptors. Judicious selection of the ligand that engages the templating protein allows appropriate effector function to be incorporated in the polymeric construct, thereby providing an opportunity for therapeutic applications. The power of this approach is exemplified by the design of exceptionally potent *Escherichia coli* Shiga toxin antagonists that protect transgenic mice that constitutively express a human pentraxin, serum amyloid P component.

- An Interfacial Oxime Reaction To Immobilize Ligands and Cells in Patterns and Gradients to Photoactive Surfaces  
Park, S.; Yousaf, M. N. *Langmuir* **2008**, *24*, 6201–6207.

Abstract :

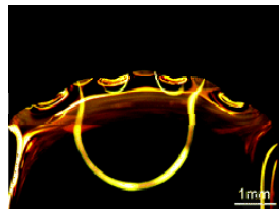


We report a molecularly controlled interfacial chemoselective methodology to immobilize ligands and cells in patterns and gradients to self-assembled monolayers on gold. This strategy is based on reacting soluble ketone or aldehyde tethered ligands to surface-bound oxyamine alkanethiols to generate a covalent oxime linkage to the surface. We characterize the kinetic behavior of the reaction on the surface with ferrocenecarboxaldehyde (FcCHO) as a model ligand. The precise extent of immobilization and therefore surface density of FcCHO on the SAM is monitored and determined by cyclic voltammetry, which shows a pseudo-first-order rate constant of  $0.13 \text{ min}^{-1}$ . In order to generate complex surface patterns and gradients of ligands on the surface, we photoprotected the oxyamine group with nitroveratryloxycarbonyl (NVOC). We show that ultraviolet light irradiation

through a patterned microfiche film reveals the oxyamine group and we characterize the rate of deprotection by immobilization of ketone containing redox active groups. Finally, we extend this strategy to show biospecific cell attachment of fibroblast cells by immobilizing ketone-GRGDS peptides in patterns. The interfacial oxime reaction is chemoselective and stable at physiological conditions (pH 7.0, 37 °C) and may potentially be used to install ligands on the surface in the presence of attached cells to modulate the cell microenvironment to generate dynamic surfaces for monitoring changes in cell behavior in real time.

- Fabrication of Multiscale Surface-Chemical Gradients by Means of Photocatalytic Lithography  
Blondiaux, N.; Zürcher, S.; Liley, M.; Spencer, N. D. *Langmuir* **2007**, *23*, 3489–3494.

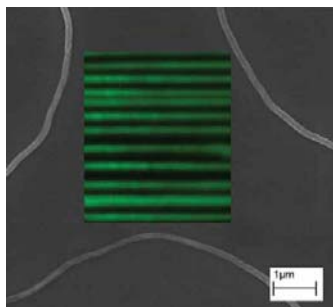
Abstract :



We describe a new method for the fabrication of surface-chemical gradients. A film of titanium dioxide is brought into close proximity to a uniformly monolayer-covered surface and exposed to UV light to produce oxygen radicals. The use of a graded grayscale mask between the UV source and the TiO<sub>2</sub> allows the production of surface-chemical gradients via oxidation of the monolayer. The technique is demonstrated on gold surfaces bearing alkanethiol SAMs. Oxidation and subsequent replacement of the oxidized thiols has been used to produce surface-chemical gradients with lengths on the submillimeter to centimeter scales. The oxidation, removal, and replacement of the thiols during the process have been demonstrated by means of XPS. This oxidative process may be applied to other surface chemistries. Similarly, other shapes and slopes of gradients may be produced, depending on the photomask employed.

- Fabrication of Multiscale Surface-Chemical Gradients by Means of Photocatalytic Lithography  
De Marco, C.; Mele, E.; Camposeo, A.; Stabile, R.; Cingolani, R.; Pisignano, D. *Adv. Mater.* **2008**, *20*, 4158–4162.

Abstract :



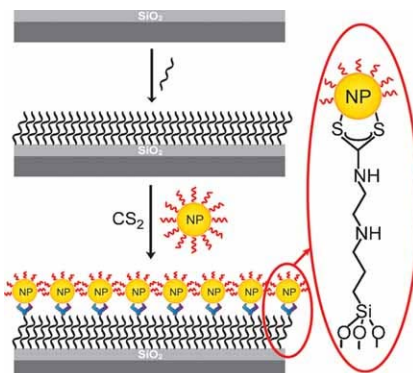
**Solvent-resistant nanofluidics** is demonstrated as sub-100-nm technology for fabricating organic light-emitting fibers, with superior control over diameter and spatial arrangement. Nanofluidics is carried out with optimal resistance to organic solvents commonly employed to dissolve conjugated polymers. The optically active nanofibers, with diameters around 60 nm, are found to exhibit photoluminescence emission polarized along their axis.



- Nanoparticle Immobilization on Surfaces via Activatable Heterobifunctional Dithiocarbamate Bond Formation  
Park, M.-H.; Ofir, Y.; Samanta, B.; Arumugam, P.; Miranda, O. R.; Rotello, V. M. *Adv. Mater.* **2008**, *20*, 4185–4188.

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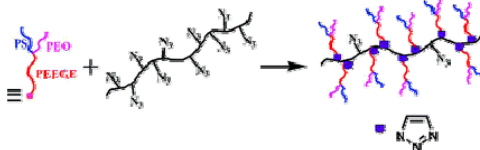
Abstract :



**A simple and reliable technique** has been developed to deposit robust monolayers of different types of nanoparticles including gold, iron-platinum, and core/shell CdSe/ZnS, using in situ dithiocarbamate formation.

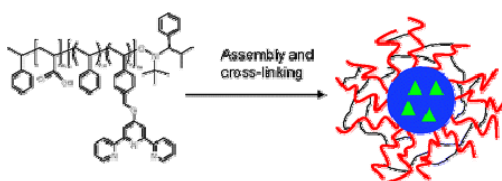
- Synthesis of a Novel Kind of Amphiphilic Graft Copolymer with Miktoarm Star-Shaped Side Chains  
Luo, X.; Wang, G.; Pang, X.; Huang, J. *Macromolecules* **2008**, *41*, 2315–2317.

Abstract :



- Synthesis of Core Functionalized Polymer Micelles and Shell Cross-Linked Nanoparticles  
Levins, A. D.; Wang, X.; Moughton, A. O.; Skey, J.; O'Reilly, R. K. *Macromolecules* **2008**, *41*, 2998–3006.

Abstract :



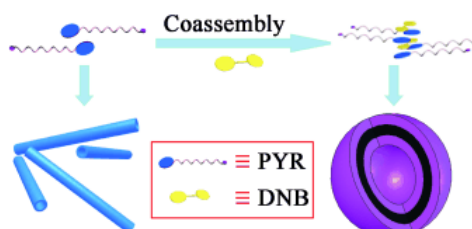
We present the synthesis of novel core reactive spherical polymeric micelles and nanoparticles using nitroxide mediated polymerization (NMP) techniques. These nanostructures have terpyridine functionality selectively located within their hydrophobic core domain and have been further modified by metal complexation (with Fe, Ru, and Cu) within this domain to afford novel metal functionalized polymer nanostructures. The hydrodynamic diameters ( $D_h$ ) of these micelles and hybrid nanoparticles were determined by dynamic light scattering (DLS), and the dimensions of the nanoparticles were characterized using transmission electron microscopy (TEM) and confirmation of the complexation was achieved using UV–vis analysis. The reactivity of the Cu-tethered metal complex within the nanostructures was investigated and was found to be an active catalyst for the 1,3-dipolar cycloaddition “click” reaction of azido and alkynyl functionalized small molecules. This

strategy provides a versatile synthetic route toward the selective incorporation of active sites within the core domain of a polymer nanoparticle.

- Controlled Self-Assembly Manipulated by Charge-Transfer Interactions: From Tubes to Vesicles

Wang, C.; Yin, S.; Chen, S.; Xu, H.; Wang, Z.; Zhang, X. *Angew. Chem. Int. Ed.* **2008**, *47*, 9049–9052.

Abstract :

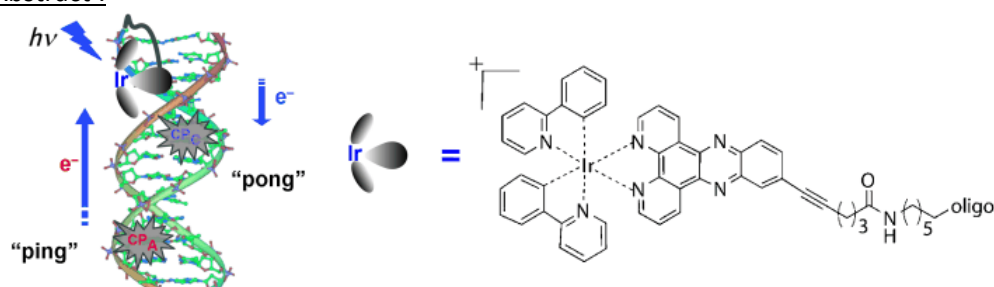


**Transfer request:** A self-assembled supramolecular charge-transfer complex of 1-(11-oxo-11-pyren-1-ylmethoxy)undecylpyridinium bromide (PYR) and ethane-1,2-diyl bis(3,5-dinitrobenzoate) (DNB) is shown to form vesicular aggregates in aqueous solution, in contrast to the tubular aggregates of pure PYR (see picture). A curvature-dependent mechanism for this change is proposed.

- Ping-Pong Electron Transfer through DNA

Elias, B.; Genereux, J. C.; Barton, J. K. *Angew. Chem. Int. Ed.* **2008**, *47*, 9067–9070.

Abstract :

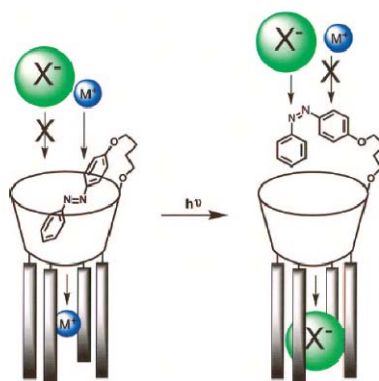


**Either way:** An Ir<sup>III</sup> complex strongly coupled to a DNA base stack can inject a hole or an electron in DNA upon irradiation (see picture). With strands containing the modified bases <sup>CP</sup>A and <sup>CP</sup>C/<sup>Br</sup>U, which serve as oxidative and reductive probes, respectively, photolysis of Ir-DNA conjugates leads to a “ping-pong” electron transfer, with both hole and electron migration.

- A Light-Gated Synthetic Ion Channel

Jog, P. V.; Gin, M. S. *Org. Lett.* **2008**, *10*, 3693–3696.

Abstract :

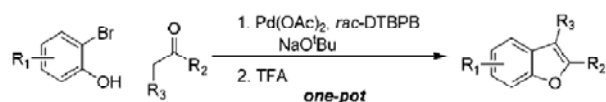


A gated synthetic ion channel with  $\beta$ -cyclodextrin as the pore and azobenzene as the gate is reported. Irradiation converts a tethered *trans*-azobenzene to *cis*-azobenzene which likely transforms the channel from a self-inclusion complex to a dissociated structure. This transformation results in an increase in anion transport and a decrease in cation transport across a phospholipid vesicle membrane.

- One-Pot Synthesis of Benzofurans via Palladium-Catalyzed Enolate Arylation with *o*-Bromophenols

Eidamshaus, C.; Burch, J. D. *Org. Lett.* **2008**, *10*, 4211–4214.

Abstract :



A one-pot synthesis of benzofurans which utilizes a palladium-catalyzed enolate arylation is described. The process demonstrates broad substrate scope and provides differentially substituted benzofurans in moderate to excellent yields. The utility of the method is further demonstrated by the synthesis of the natural product eupomatenoic acid in three steps.