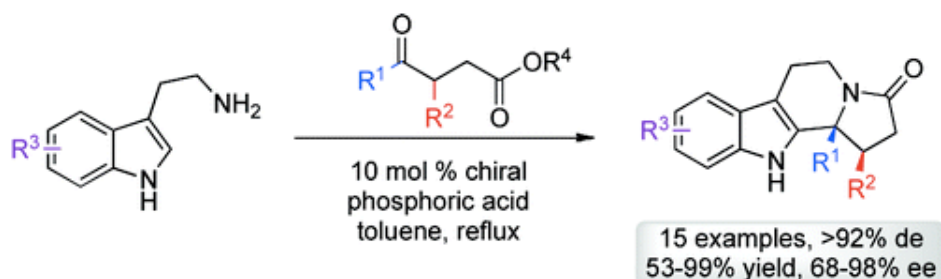


- Direct Enantioselective Brønsted Acid Catalyzed *N*-Acyliminium Cyclization Cascades of Tryptamines and Ketoacids

1

Holloway, C. A.; Muratore, M. E.; Storer, R. I.; Dixon, D. J. *Org. Lett.* **2010**, *12*, 4720-4723.

Abstract:

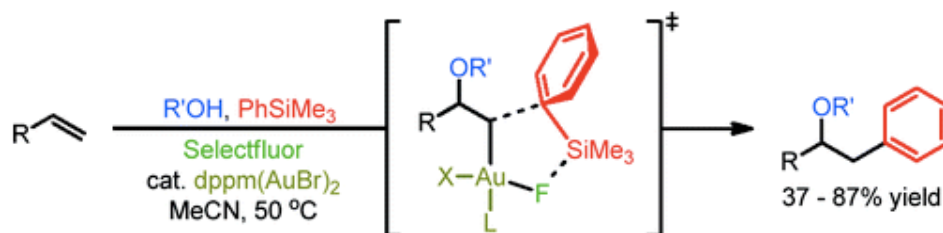


A direct enantio- and diastereoselective *N*-acyliminium cyclization cascade through chiral phosphoric acid catalyzed condensation of tryptamines with γ - and δ -ketoacid derivatives to provide architecturally complex heterocycles has been developed. The reaction is technically simple to perform, atom-efficient, and broad in scope. Employing 10 mol % of (*R*)-BINOL derived chiral phosphoric acids in refluxing toluene allowed the polycyclic product materials to be generated in good yields (53-99%) and moderate to high enantioselectivities (68-98% ee).

- Gold-Catalyzed Oxidative Coupling Reactions with Aryltrimethylsilanes

Brenzovich, Jr., W. E.; Brazeau, J.-F.; Toste, F. D. *Org. Lett.* **2010**, *12*, 4728-4731.

Abstract:

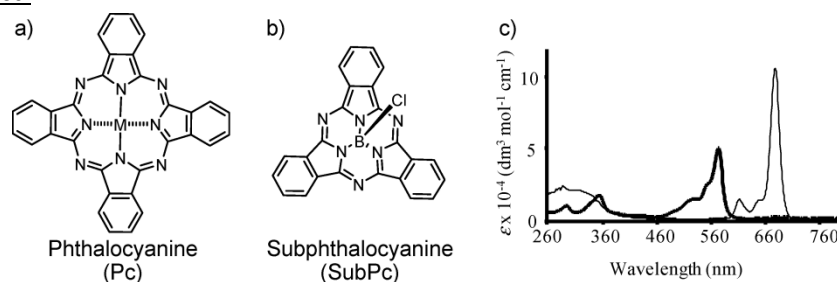


During continuing studies with a novel oxidative gold oxyarylation reaction, arylsilanes were found to be competent coupling partners, providing further evidence for an intramolecular electrophilic aromatic substitution mechanism. While providing yields complementary to those of the previously described boronic acid methods, the use of trimethylsilanes reduces the observation of homocoupling byproducts and allows for facile intramolecular coupling reactions.

- Covalent and Noncovalent Phthalocyanine–Carbon Nanostructure Systems: Synthesis, Photoinduced Electron Transfer, and Application to Molecular Photovoltaics

Bottari, G.; de la Torre, G.; Guldi, D. M.; Torres, T. *Chem. Rev.* **2010**, *110*, 6768–6816.

Abstract:



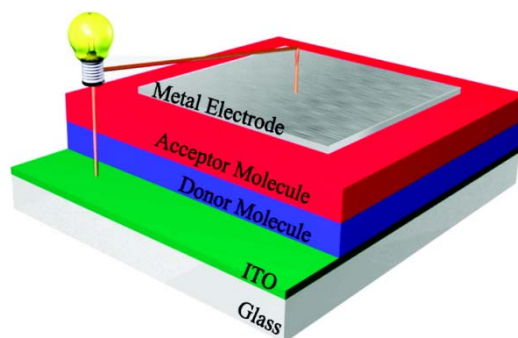
Photosynthesis is used by nature to convert light energy into chemical energy in some living systems. In such a process, a cascade of very efficient, short-range energy and electron transfer events between well-arranged, light-harvesting organic donor and acceptor pigments takes place within the photosynthetic reaction center, leading to the overall generation of chemical energy from sunlight with near quantum efficiency.

Herein, we review the different synthetic strategies that have been pursued so far for the preparation of D–A Pc– and SubPc–carbon nanostructure systems, having the donor and the acceptor units connected either covalently or by using supramolecular interactions. A photophysical analysis of most of these systems will also be presented with the aim of rationalizing which effect the structural and electronic features of these D–A systems have on the photoinduced electron/energy transfer dynamics. The utilization of Pcs and fullerenes in organic photovoltaics will be also reviewed in terms of both the different types of organic solar cell architectures and performance of the devices.

- Polyphenylene-Based Materials for Organic Photovoltaics

Li, C.; Liu, M.; Pschirer, N. G.; Baumgarten, M.; Müllen, K. *Chem. Rev.* **2010**, *110*, 6817–6855.

Abstract:



In considering the uniqueness of polyphenylene-based materials, the present article focuses on organic semiconductors and sensitizers obtained when using benzene as a regular building block. This review is divided into three parts.

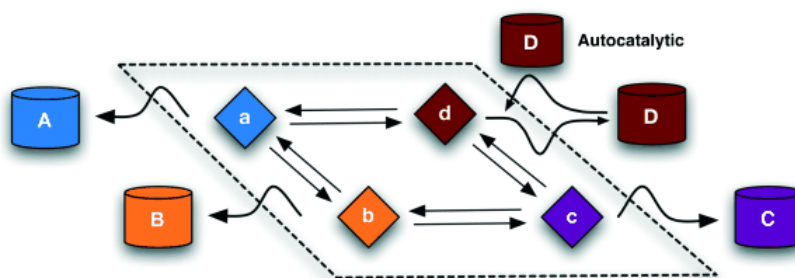
The first part provides a general introduction to different cell structures and their practical characterizations, including flat-heterojunction, bulk-heterojunction, and dye-sensitized solar cells.

In the second part, the focus is on polyphenylene-based materials. It first describes one-dimensional polyphenylenes or oligophenylene rod-type compounds, then 2D polyphenylenes (especially perylenes and their derivatives), and finally polyphenylene dendrimers. Moreover, this section includes the application and performance of these materials in photovoltaics. The conjugated polyphenylenes are mainly applicable to bulk-heterojunction polymer solar cells, while the conjugated oligomers with donor–acceptor end groups are primarily employed in dye-sensitized solar cells. With their facile functionalization, extraordinary absorption, as well as photostability, the application of perylenes and their derivatives covers all types of solar cells. Finally this second section concludes with a description of multichromophoric dendrimers and the concept of single-molecular level light-harvest systems.

The third part of the paper provides a conclusion as well as an outlook.

- Integrating Replication-Based Selection Strategies in Dynamic Covalent Systems
del Amo, V.; Philp, D. *Chem.-Eur. J.* **2010**, *16*, 13304-13318.

Abstract:

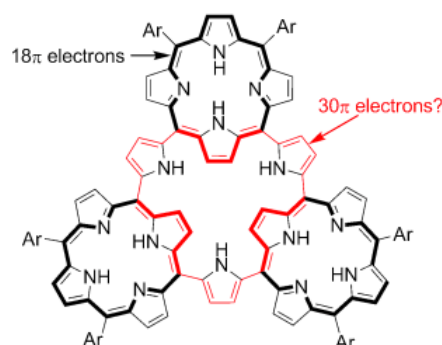


In the past 15 years, the chemistry of reversible covalent bond formation (dynamic covalent chemistry (DCC)) has been exploited to engineer networks of interconverting compounds known as dynamic combinatorial libraries (DCLs). Classically, the distribution of library components is governed by their relative free energies, and so, processes that manipulate the free energy landscape of the DCL can influence the distribution of library members. Within the same time frame, the design and implementation of molecules capable of copying themselves—so-called replicators—has emerged from the field of template-directed synthesis. Harnessing the nonlinear kinetics inherent in replicator behavior offers an attractive strategy for amplification of a target structure within a DCL and, hence, engendering high levels of selectivity within that library. The instructional nature of replicating templates also renders the combination of replication and DCC a potential vehicle for developing complex reaction networks; a prerequisite for the development of the emerging field of systems chemistry. This Concept article explores the role of kinetically and thermodynamically controlled processes within different DCC frameworks. The effects of embedding a replicating system within these DCC frameworks is explored and the consequences of the different topologies of the reaction network for amplification and selectivity within DCLs is highlighted.

- Pyrrole-Bridged Porphyrin Nanorings

Song, J.; Aratani, N.; Shinokubo, H.; Osuka, A. *Chem.-Eur. J.* **2010**, *16*, 13320-13324.

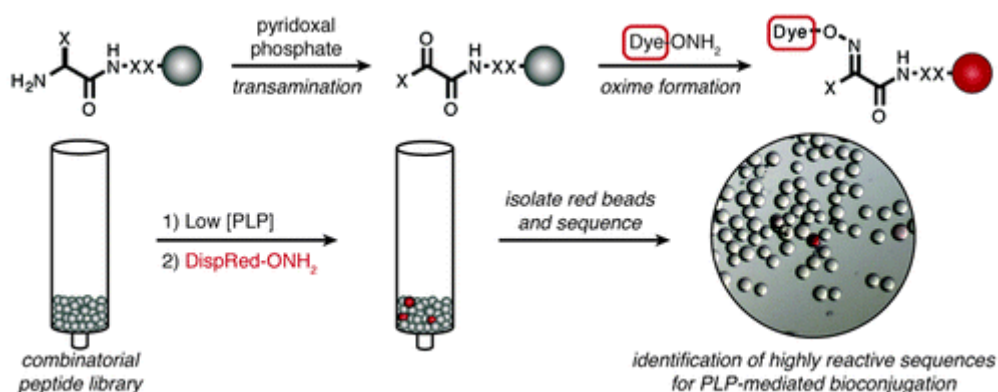
Abstract:



Bridging the gap: A series of meso-to-meso pyrrole-bridged cyclic porphyrins were prepared by a one-pot Suzuki–Miyaura coupling reaction (see figure). The ^1H -NMR spectra of these compounds revealed their highly symmetric structures in solution, and the solid-state structures of nickel and zinc derivatives were determined by X-ray crystal analysis. The UV/Vis absorption spectra of the cyclic arrays indicate the strong excitonic interactions among porphyrins.

- Identification of Highly Reactive Sequences For PLP-Mediated Bioconjugation Using a Combinatorial Peptide Library

Witus, L. S.; Moore, T.; Thuronyi, B. W.; Kahn, A. P. E.; Scheck, R. A.; Iavarone, A. T.; Francis, M. B. *J. Am. Chem. Soc.* **2010**, *132*, 16812–16817.

Abstract:

Chemical reactions that facilitate the attachment of synthetic groups to proteins are useful tools for the field of chemical biology and enable the incorporation of proteins into new materials. We have previously reported a pyridoxal 5'-phosphate (PLP)-mediated reaction that site-specifically oxidizes the N-terminal amine of a protein to afford a ketone. This unique functional group can then be used to attach a reagent of choice through oxime formation. Since its initial report, we have found that the N-terminal sequence of the protein can significantly influence the overall success of this strategy. To obtain short sequences that lead to optimal conversion levels, an efficient method for the evaluation of all possible N-terminal amino acid combinations was needed. This was achieved by developing a generalizable combinatorial peptide library screening platform suitable for the identification of sequences that display high levels of reactivity toward a desired bioconjugation reaction. In the context of N-terminal transamination, a highly reactive alanine-lysine motif emerged, which was confirmed to promote the modification of peptide substrates with PLP. This sequence was also tested on two protein substrates, leading to substantial increases in reactivity relative to their wild-type termini. This readily encodable tripeptide thus appears to provide a significant improvement in the reliability with which the PLP-mediated bioconjugation reaction can be used. This study also provides an important first example of how synthetic peptide libraries can accelerate the discovery and optimization of protein bioconjugation strategies.

- **Supramolecular Balance: Using Cooperativity To Amplify Weak Interactions**
Roman, M.; Cannizzo, C.; Pinault, T.; Isare, B.; Andrioletti, B.; Schoot, P.; Bouteiller, L. *J. Am. Chem. Soc.* **2010**, *132*, 16818–16824.

Abstract:

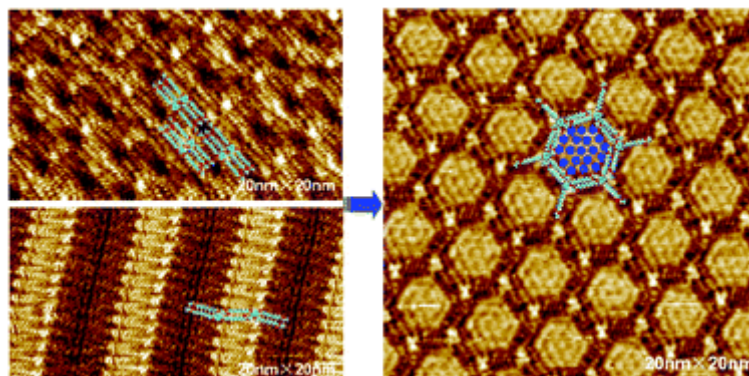
Gathering precise knowledge on weak supramolecular interactions is difficult yet is of utmost importance for numerous scientific fields, including catalysis, crystal engineering, ligand binding, and protein folding. We report on a combined theoretical and experimental approach showing that it is possible to vastly improve the sensitivity of current methods to probe weak supramolecular interactions in solution. The concept consists of using a supramolecular platform involving a highly

cooperative configurational transition, the perturbation of which (by the modification of the molecular building blocks) can be monitored in a temperature scanning experiment. We tested this concept with a particular bisurea platform, and our first results show that it is possible to detect the presence of interaction differences as low as 60 J/mol, which may be due to steric repulsion between vinyl and alkyl groups or may be the result of solvation effects.

- Tuning the packing density of host molecular self-assemblies at the solid–liquid interface using guest molecule

Miao, X.; Xu, L.; Li, Y.; Li, Z.; Zhou, J.; Deng, W. *Chem. Commun.* **2010**, *46*, 8830–8832.

Abstract:

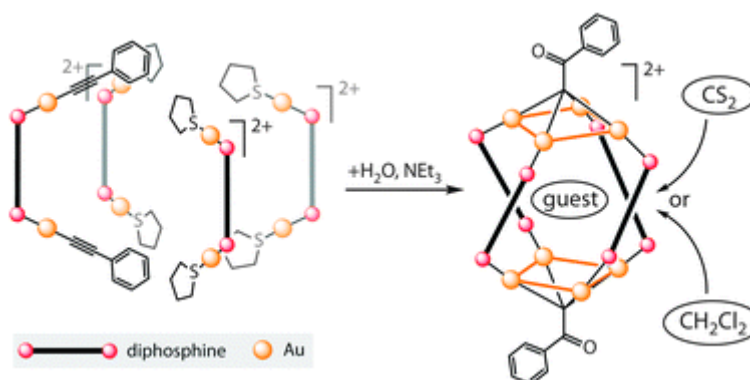


The use of THB molecules as a guest template tunes the formation of a two-dimensional honeycomb network in preference to alternative close packed structures of TECDB self-assembled on HOPG surface at the solid–liquid interface.

- Assembly of the Au–diphosphine helical cage molecules via alkynyl– μ_4 -methylidyne ligand transformation

Koshevoy, I. O.; Haukka, M.; Selivanov, S. I.; Tunik, S. P.; Pakkanen, T. A. *Chem. Commun.* **2010**, *46*, 8926–8928.

Abstract:

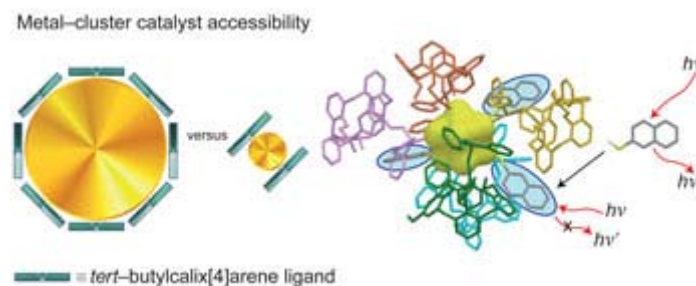


The assembly of the gold(I)–diphosphine cages occurs via unprecedented transformation of the alkynyls into the μ_4 -methylidyne ligands under basic conditions. These compounds demonstrate the equilibrium between the P \leftrightarrow M helical isomers and serve as hosts to accommodate small molecules (CH_2Cl_2 and CS_2).

- A bioinspired approach for controlling accessibility in calix[4]arene-bound metal cluster catalysts

de Silva, N.; Ha, J.-M.; Solovyov, A.; Nigra, M. M.; Ogino, I.; Yeh, S. W.; Durkin, K. A.; Katz, A. *Nature Chemistry* **2010**, *2*, 1062–1068.

Abstract:

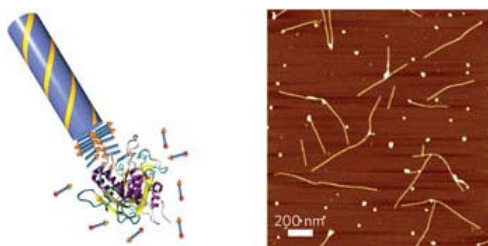


In enzymes, the electronic and steric environments of active centres, and therefore their activity in biological processes, are controlled by the surrounding amino acids. In a similar manner, organic ligands have been used for the ‘passivation’ of metal clusters, that is, inhibition of their aggregation and control of their environment. However, the ability of enzymes to maintain large degrees of accessibility has remained difficult to mimic in synthetic systems in which little room, if any, is typically left to bind to other species. Here, using calix[4]arene macrocycles bearing phosphines as crude mimics of the rigid backbones of proteins, we demonstrate the synthesis of gold clusters and the control of their accessibility through an interplay between the sizes of the calixarene ligands and metal cores. For 0.9-nm cores, 25% of all the gold atoms within the cluster bind to the chemisorption probe 2-naphthalenethiol. This accessibility dramatically decreases with 1.1-nm and 4-nm gold cores.

- Biocatalytic induction of supramolecular order

Hirst, A. R.; Roy, S.; Arora, M.; Das, A. K.; Hodson, N.; Murray, P.; Marshall, S.; Javid, N.; Sefcik, J.; Boekhoven, J.; van Esch, J. H.; Santabarbara, S.; Hunt, N. T.; Ulijn, R. V. *Nature Chemistry* **2010**, *2*, 1089–1094.

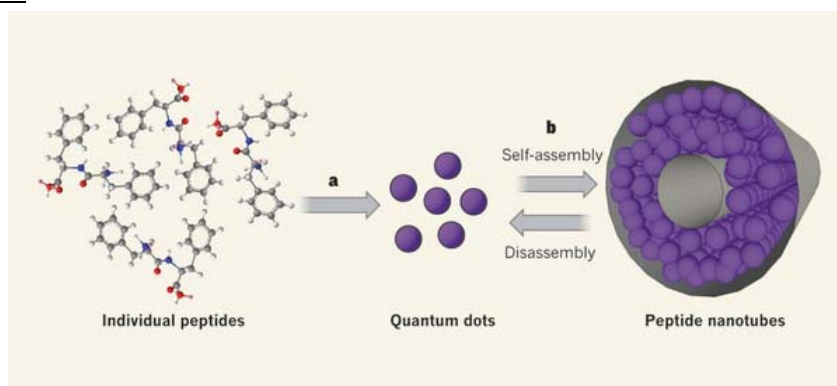
Abstract:



Supramolecular gels, which demonstrate tunable functionalities, have attracted much interest in a range of areas, including healthcare, environmental protection and energy-related technologies. Preparing these materials in a reliable manner is challenging, with an increased level of kinetic defects observed at higher self-assembly rates. Here, by combining biocatalysis and molecular self-assembly, we have shown the ability to more quickly access higher-ordered structures. By simply increasing enzyme concentration, supramolecular order expressed at molecular, nano- and micro-levels is dramatically enhanced, and, importantly, the gelator concentrations remain identical. Amphiphile molecules were prepared by attaching an aromatic moiety to a dipeptide backbone capped with a methyl ester. Their self-assembly was induced by an enzyme that hydrolysed the ester. Different enzyme concentrations altered the catalytic activity and size of the enzyme clusters, affecting their mobility. This allowed structurally diverse materials that represent local minima in the free energy landscape to be accessed based on a single gelator structure.

- Nanotechnology: Peptides as biological semiconductors
Hauser, C. A. E.; Zhang, S. *Nature* **2010**, *468*, 516–517.

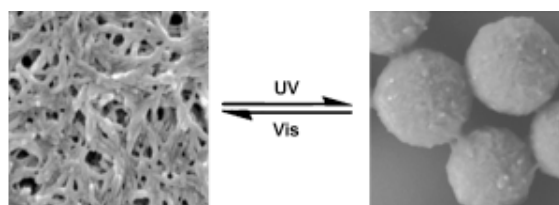
Abstract:



Could a simple, short peptide made of naturally occurring amino acids form structures that have the optical and electronic properties of semiconductor nanocrystals? Reporting in the *Journal of the American Chemical Society*, Gazit, Rosenman and colleagues describe a peptide formed from just two phenylalanine amino acids that does exactly that. This is a remarkable discovery, because although conductive organic polymers are well known (their discoverers won the 2000 Nobel chemistry prize), no one had envisaged that biological peptides could act as semiconductors. The reported dipeptide assemblies represent an intriguing, bioorganic class of 'quantum dot' nanomaterial.

- Smart Self-Assemblies Based on a Surfactant-Encapsulated Photoresponsive Polyoxometalate Complex
Yan, Y.; Wang, H.; Li, B.; Hou, G.; Yin, Z.; Wu, L.; Yam, V. W. W. *Angew. Chem. Int. Ed.* **2010**, *49*, 9233-9236.

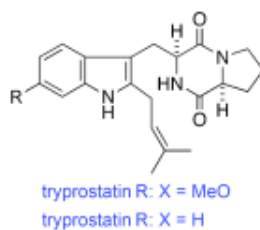
Abstract:



Smart POMs: A surfactant-encapsulated organic-grafted polyoxometalate (POM) is synthesized by grafting a photoresponsive azobenzene group to an Anderson-type POM cluster. Self-assemblies of the hybrid complexes exhibit photocontrolled reversible aggregation and morphological change as a result of photoisomerization-induced structural alternation (see figure).

- Total Synthesis of Tryprostatins A and B
Yamakawa, T.; Ideue, E.; Shimokawa, J.; Fukuyama, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 9262-9265.

Abstract:

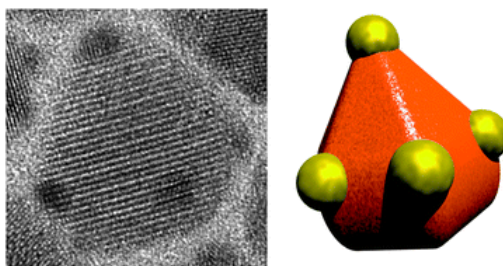


A reasonable approach to the radical: The establishment of reliable conditions for the radical-mediated construction of indoles enabled the highly efficient synthesis of tryprostatins A and B. Use of the radical initiator 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) has allowed to carry out the radical cyclization at just 30 °C, thereby suppressing the formation of by-products.

- Growth and reductive transformation of a gold shell around pyramidal cadmium selenide nanocrystals

Meyns, M.; Bastus, N. G.; Cai, Y.; Kornowski, A.; Juárez, B. H.; Weller, H.; Klinke, C. *J. Mater. Chem.* **2010**, *20*, 10602-10605.

Abstract:

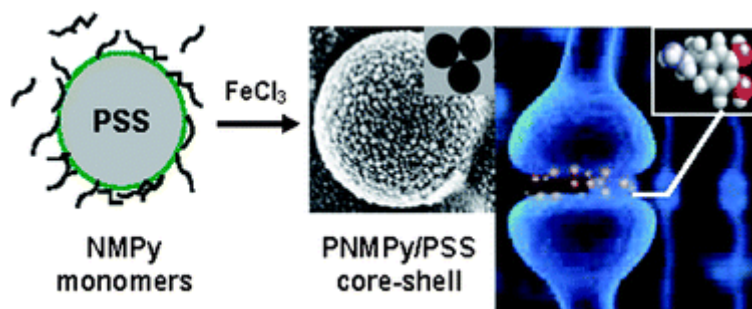


We report the growth of an unstable shell-like gold structure around dihexagonal pyramidal CdSe nanocrystals in organic solution and the structural transformation to spherical domains by two means: (i) electron beam irradiation (*in situ*) and (ii) addition of a strong reducing agent during synthesis. By varying the conditions of gold deposition, such as ligands present or the geometry of the CdSe nanocrystals, we were able to tune the gold domain size between 1.4 nm and 3.9 nm and gain important information on the role of surface chemistry in heteronanoparticle synthesis and seed reactivity, both of which are crucial points regarding the chemical design of new materials for photocatalysis and optoelectronic applications.

- Nanostructured conducting polymer for dopamine detection

Martí, M.; Fabregat, G.; Estrany, F.; Alemán, C.; Armelin, E. *J. Mater. Chem.* **2010**, *20*, 10652-10660.

Abstract:



In this work, we demonstrate the ability of poly(*N*-methylpyrrole) to form nanostructures and to detect very low concentrations of dopamine, an important neurotransmitter. Poly(*N*-methylpyrrole)

hollow particles of controlled thickness have been prepared using the layer-by-layer assembly technique and polystyrene core-shell particles as templates, which are subsequently eliminated to yield free-standing hollow microspheres with a layer thickness of 30 nm. The morphology and composition of these structures have been evaluated by scanning electron microscopy, transmission electron microscopy, FTIR, Raman and X-ray photoelectron spectroscopies. Results demonstrate that intact hollow spheres can be obtained controlling the number of polymer deposition cycles. Furthermore, two kind of sensors were constructed by immobilizing poly(*N*-methylpyrrole)/Au nanocomposites and poly(*N*-methylpyrrole) nanomembranes on the surface of a glassy carbon electrode. Electrochemical techniques were employed to evaluate the ability of poly(*N*-methylpyrrole) to absorb/immobilize dopamine molecules. It was found that systems based on this conducting polymer are highly sensitive to the neurotransmitter concentration, presenting a very fast response even when the concentration of the dopamine is very low.

- Polymerization of Naturally Renewable Methylene Butyrolactones by Half-Sandwich Indenyl Rare Earth Metal Dialkyls with Exceptional Activity
Hu, Y.; Xu, X.; Zhang, Y.; Chen, Y.; Chen, E. Y.-X. *Macromolecules* **2010**, *43*, 9328–9336.

Abstract:

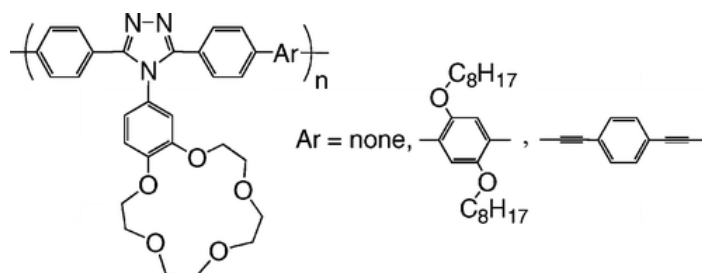


Four discrete half-sandwich dialkyl rare earth metal (REM) complexes incorporating a disilylated indenyl ligand, $(1,3-(\text{SiMe}_3)_2\text{C}_9\text{H}_5)\text{M}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ ($\text{M} = \text{Sc}, \text{Y}, \text{Dy}, \text{Lu}$), have been investigated for the coordination–addition polymerization of naturally renewable methylene butyrolactones, α -methylene- γ -butyrolactone (MBL) and γ -methyl- α -methylene- γ -butyrolactone (MMBL). Initial screening for the polymerization of methyl methacrylate highlighted several differences in catalytic behavior between these half-sandwich REM catalysts and well-studied sandwich REM catalysts in terms of reactivity trend, polymer tacticity, and solvent dependence. Most significantly, all four catalysts herein exhibit exceptional activity for polymerization of MMBL in DMF, achieving quantitative monomer conversion in <1 min with a 0.20 mol % catalyst loading and giving a high turnover frequency of $>30\,000\text{ h}^{-1}$. Slower polymerizations occur in CH_2Cl_2 , allowing for establishment of the activity trend within this REM series, which follows: Dy (largest ion) \geq Y $>$ Lu $>$ Sc (smallest ion). The most active and effective Dy catalyst has been examined in detail, demonstrating its ability to control the polymerization for producing PMMBL with high T_g (221 °C) and with molecular weight ranging from a medium M_n of 1.89×10^4 Da to a high M_n of 1.63×10^5 Da, programmed by the $[\text{MMBL}]/[\text{Dy}]$ ratio. Kinetic experiments have revealed a first-order dependence on $[\text{monomer}]$ and a second-order dependence on $[\text{REM}]$. These kinetic results, coupled to catalyst efficiencies, NMR studies, as well as with chain-end group analysis by MALDI-TOF mass spectrometry, have yielded a chain initiation mechanism that involves both alkyl groups on each metal center and a bimolecular chain propagation that involves two metal centers in the rate-limiting C–C bond forming step. The Dy catalyst response to enolizable organo acids, externally added as chain-transfer agents, has also been examined.

- Synthesis of n-Type π -Conjugated Polymers with Pendant Crown Ether and Their Stability of n-Doping State against Air

Yamaguchi, I.; Mitsuno, H. *Macromolecules* **2010**, *43*, 9348–9354.

Abstract:



The n-type π -conjugated polymers with a 1,2,4-triazole ring substituted by a benzo-15-crown-5-ether (benzo15C5) subunit at the 4-position of the 1,2,4-triazole ring were synthesized by organometallic polycondensations. The UV-vis spectra of the polymers exhibited absorption maxima (λ_{\max} values) at a longer wavelength than that exhibited by 4-benzo15C5-1,2,4-triazole (model-1), revealing that their π -conjugation system was expanded along the polymer chain. The electric conductivity measurements suggested that model-1 formed inclusion adducts with 1:1 and 2:1 molar ratios with Na^+ and K^+ , respectively. Addition of KClO_4 to the DMSO solutions of the polymers with the benzo15C5 subunit caused the formation of the 2:1 inclusion between the 15C5 ring and K^+ ; this inclusion led to a bathochromic shift in λ_{\max} of the polymers. In addition, photoluminescence intensity of the polymers decreased after the addition of KClO_4 to solution. The polymers with the benzo15C5 subunit underwent an electrochemical reduction (n-doping), and the corresponding oxidation (n-dedoping) occurred at an unusually high potential in an acetonitrile solution of NaClO_4 ; the factor responsible for the unusually high oxidation potential was the stabilized n-doping state that was attributed to the inclusion of Na^+ in the 15C5 ring. The electric conductivities of the polymers were increased by n-doping with sodium naphthalenide. The polymers with the benzo15C5 subunit exhibited a considerably higher stability of the n-doping state in air than did those without this subunit.