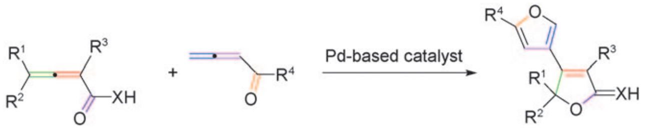
CONTENTS

CONCEPTS

Cross-Coupling

B. Alcaide, P. Almendros,* T. Martínez del Campo* ..... 5836 – 5842

Cross-Coupling/Cyclization Reactions of Two Different Allenic Moieties



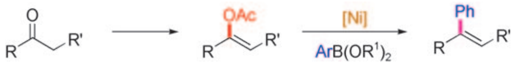
Simple and practical: The heterocyclization, palladium-catalyzed cross-coupling reaction of two different allene moieties (see scheme) is a selective and powerful method for the direct synthesis of functionalized heterocycles of biological interest, namely, butenolides, furanimines, and 2,5-dihydrofuran derivatives.

COMMUNICATIONS

Cross-Coupling

*C.-L. Sun, Y. Wang, X. Zhou, Z.-H. Wu, B.-J. Li, B.-T. Guan, Z.-J. Shi** .... 5844 – 5847

Construction of Polysubstituted Olefins through Ni-Catalyzed Direct Activation of Alkenyl C−O of Substituted Alkenyl Acetates

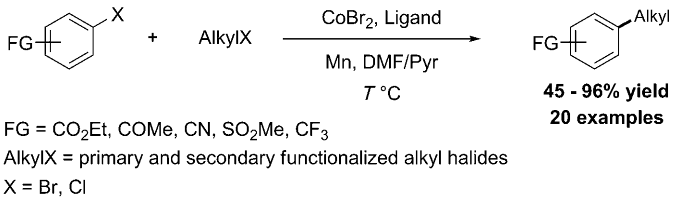


Reliable companion: For the first time cross-coupling between alkenyl acetates and arylboroxines/PhZnCl has been developed via Ni catalysis. Alkenyl acetates could be well-differentiated from aryl acetates (see scheme). This reliable method provides a convenient pathway to construct polysubstituted styrene derivatives.

Cross-Coupling

*M. Amatore, C. Gosmini** .. 5848 – 5852

Direct Method for Carbon–Carbon Bond Formation: The Functional Group Tolerant Cobalt-Catalyzed Alkylation of Aryl Halides

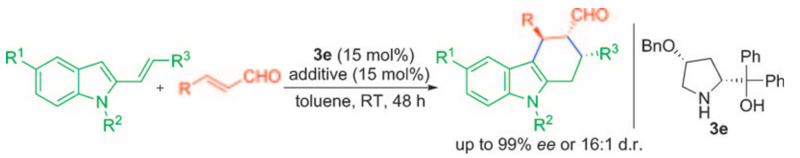


A new protocol for the direct cobalt-catalyzed alkylation of aryl halides has been developed that proceeds smoothly in the presence of phosphanes or bipyridines as ligands with a variety of alkyl halides, including challenging alkyl electrophiles bearing β-hydrogen atoms (see scheme). Sensitive functional groups are tolerated on both coupling partners, thus, significantly extending the general scope of transition-metal-catalyzed alkylation of aryl halides.

Asymmetric Synthesis

*C. W. Zheng, Y. P. Lu, J. K. Zhang, X. K. Chen, Z. Chai, W. Y. Ma, G. Zhao** .... 5853 – 5857

The Enantioselective, Organocatalyzed Diels–Alder Reaction of 2-Vinylindoles with α,β-Unsaturated Aldehydes: An Efficient Route to Functionalized Tetrahydrocarbazoles



Prolinol catalysts: A highly enantio- and diastereoselective prolinol-catalyzed Diels–Alder reaction of 2-vinylindoles and α,β-unsaturated aldehydes is developed (see scheme). This methodology allows the development of further applications of prolinols in asymmetric synthesis. The resulting densely functionalized enantiomerically pure tetrahydrocarbazoles are useful in the total synthesis of natural products such as the core structure of the akuammiline alkaloid vincorine.

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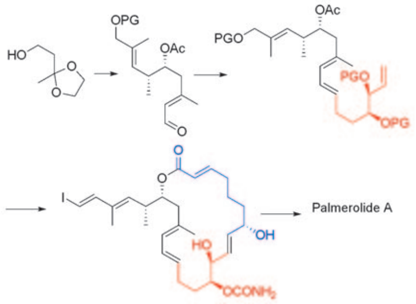
Natural Products

P. Gowrisankar, S. A. Pujari,
*K. P. Kaliappan** 5858–5862

A Formal Total Synthesis of Palmerolide A

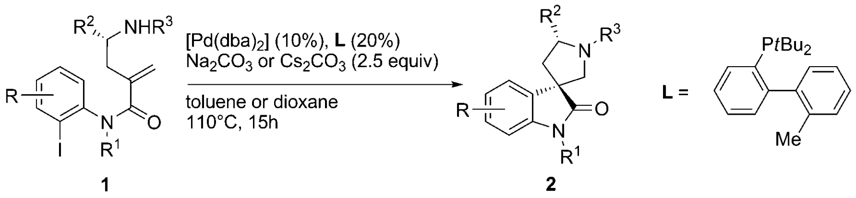


Under the sea: An efficient formal total synthesis of the marine natural product palmerolide A is reported herein, involving 24 longest linear steps. The key features of our synthesis involve a combination of Sharpless epoxidation and Shimizu reaction to construct the *syn* aldol moiety, a Julia–Kocienski reaction to construct the diene, and ring-closing metathesis to form the macrocycle (see scheme; PG = protecting group).

Aminopalladation

S. Jaegli, W. Erb, P. Retailleau,
*J.-P. Vors, L. Neuville,**
*J. Zhu** 5863–5867

Palladium-Catalyzed Domino Process to Spirooxindoles: Ligand Effect on Aminopalladation versus Carbopalladation

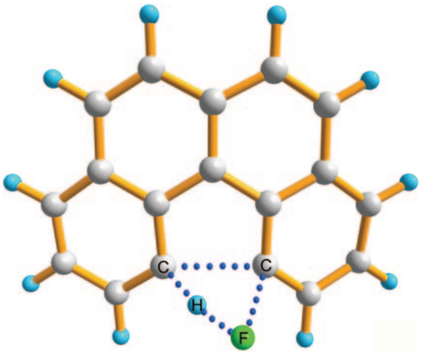


Double intra, from linear to spiro: A Pd-catalyzed domino sequence involving an intramolecular aminopalladation followed by arylation that convert linear anilides **1** into the functionalized spiropyrrolidine-3,3′-oxindoles **2** in good to excellent yields is presented. The use of 2-di-*tert*-butylphosphino-2′-methylbiphenyl as a ligand determines the success of the domino process. A *trans*-aminopalladation mechanism seems to account for the observed diastereoselectivity.

C−C Coupling

K. Y. Amsharov, M. A. Kabdulov,*
M. Jansen 5868–5871

Homo-elimination of HF—An Efficient Approach for Intramolecular Aryl–Aryl Coupling

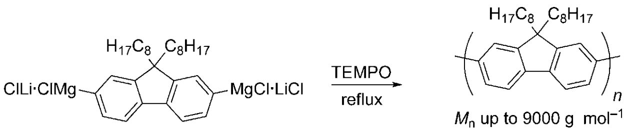


A process of elimination: The through-space fluorine activation in the benzo[*c*]phenanthrene cyclisation process has been examined experimentally and confirmed theoretically (see figure). Thermally provoked HF homo-elimination was found to be an efficient approach for selective intramolecular aryl–aryl coupling. The data obtained provide new prospects for the synthesis of non-planar aromatic hydrocarbons and fullerenes employing the flash vacuum pyrolysis technique.

Polymerization

M. S. Maji, T. Pfeifer,
*A. Studer** 5872–5875

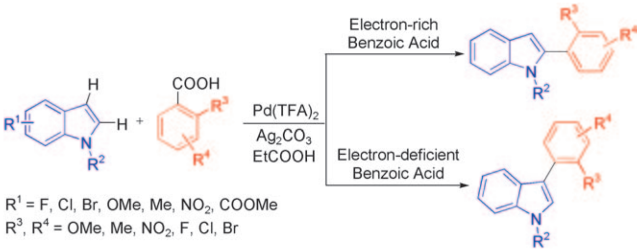
Transition-Metal-Free Synthesis of Conjugated Polymers from Bis-Grignard Reagents by Using TEMPO as Oxidant



Increasing the TEMPO! Transition metals are not necessary for oxidative polymerization of 2,7-di-magnesated fluorenes. Oxidation readily occurs by using the commercially available 2,2,6,6-tetramethyl-piperine 1-oxyl radical (TEMPO) as an oxidant. Polyfluorenes with M_n of up to 9000 $g\,mol^{-1}$ can be obtained (see scheme).

Cross-Coupling

A Versatile Catalyst for Intermolecular Direct Arylation of Indoles with Benzoic Acids as Arylating Reagents

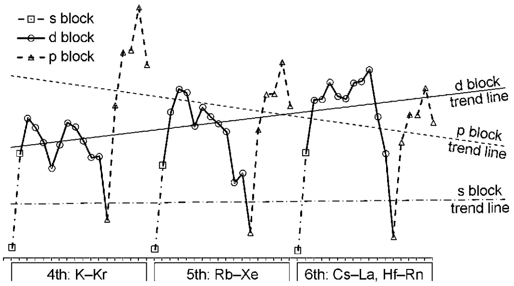


Coupled together: With a versatile catalyst system (Pd(TFA)$_2$/Ag$_2$CO$_3$/propionic acid) both electron-rich and -deficient benzoic acids serve as arylating reagents for the direct functionalization of a wide rage of indoles by a combination of decarboxylation and C–H bond activation. Depending on the nature of the benzoic acids, the reaction occurs selectively at either the C2- or C3-position of indoles, which may arise from two different catalytic pathways (see scheme; TFA = trifluoroacetate).

FULL PAPERS

Bond Dissociation Energy

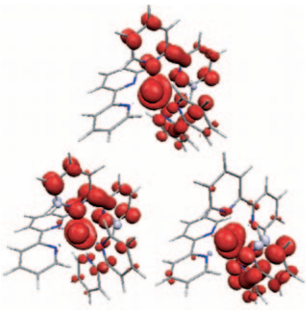
Bonding in Cationic MCH$_2^+$ (M = K–La, Hf–Rn): A Theoretical Study on Periodic Trends



To bind or not to bind: A DFT analysis of 54 cationic methylene complexes MCH$_2^+$ (M = K–La, Hf–Rn) reveals different bonding trends for s-, p-, and d-block elements (see figure).

Photophysics

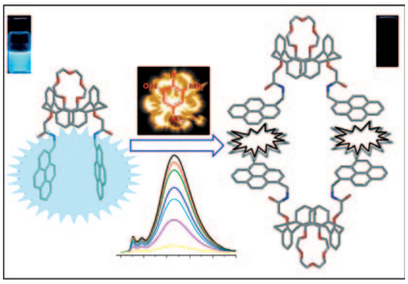
Electron Localization Dynamics in the Triplet Excited State of [Ru(bpy)$_3$]$^{2+}$ in Aqueous Solution



Electrons that can leap frog! A solvent-induced breaking of the coordination symmetry with consequent localization of the photoexcited electron on one or two bipyridine units in [Ru(bpy)$_3$]$^{2+}$ is reported (bpy = 2,2′-bipyridine; see figure). Frequent electronic "hops" between these "pairs" of ligands are observed with a characteristic time of approximately half a picosecond.

Sensors

Dipyrenylcalix[4]arene—A Fluorescence-Based Chemosensor for Trinitroaromatic Explosives



How to find TNT! A new chemosensor-based approach for the detection of nitrated aromatics is described. It involves the analyte-induced quenching of excimer emission of a dipyrenylcalix[4]-arene (**L**; see graphic). In the solid state, the complex **L**·TNT consists of a supramolecular crystalline polymeric structure, the formation of which appears to be driven by intermolecular π–π interactions between two pyrene units and a TNT molecule held at a distance of 3.2–3.6 Å.

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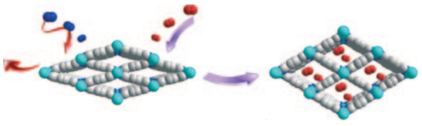
Porous Materials

*A. Demessence,
J. R. Long** .... 5902 – 5908

Selective Gas Adsorption in the Flexible Metal–Organic Frameworks Cu(BDTri)L (L = DMF, DEF)

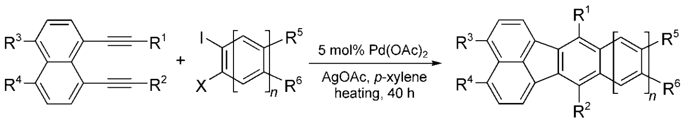


And breathe! Two isostructural copper(II)-based frameworks have been synthesized with the newly developed ligand 1,4-benzenedi(1,2,3-triazole) (H_2BDTri). Both microporous flexible metal–organic frameworks exhibit one-dimensional channels with a bridging solvent molecule, dimethyl- or diethylformamide, pointing inside the pores. Depending on the solvent molecule and the adsorbed gas, a selective pore-opening process is observed (see figure).

Cross-Coupling

Y.-H. Kung, Y.-S. Cheng, C.-C. Tai, W.-S. Liu, C.-C. Shin, C.-C. Ma, Y.-C. Tsai, T.-C. Wu, M.-Y. Kuo, Y.-T. Wu** .... 5909 – 5919

Synthesis, Structures, and Physical Properties of Benzo[*k*]fluoranthene-Based Linear Acenes

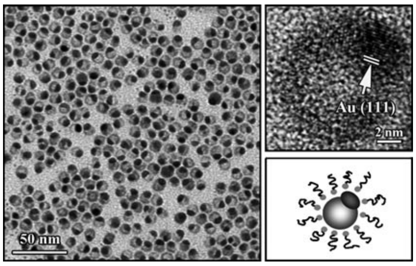


Linear acenes: Benzo[*k*]fluoranthene-based linear acenes (see graphic) are accessible through Pd-catalyzed cycloadditions between 1,8-diethynylnaphthalene derivatives and aryl iodides. The aromatic π systems in some of them are not extended as efficiently as might be expected and affected their physical properties. Most of these cycloadducts display interesting luminescence properties.

Gold Nanostructures

S. Huang, J. Huang, J. Yang, J.-J. Peng, Q. Zhang, F. Peng, H. Wang, H. Yu* .... 5920 – 5926

Chemical Synthesis, Structure Characterization, and Optical Properties of Hollow PbS_x–Solid Au Heterodimer Nanostructures

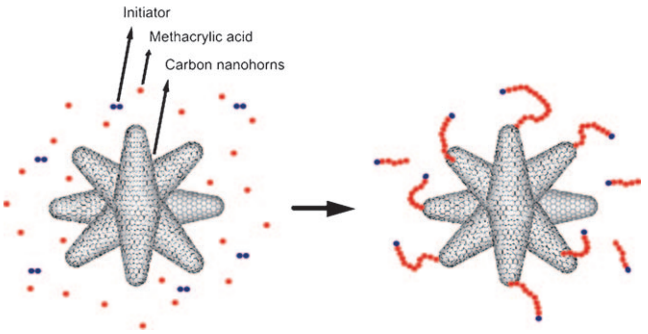


Solid gold: Solid heterodimer nanostructures exhibiting an increasing degree of complexity and functionality are highly desirable in many fields. So far, all heterodimer nanostructures are constructed of solid building units. Herein, nearly monodisperse heterodimer nanostructures (see picture) based on hollow PbS_x and solid Au have been synthesized by a mild reaction between PbS nanocrystals and the gold precursor in the presence of dodecylamine.

Nanoparticles

G. Mountrichas, S. Pispas, T. Ichihasi, M. Yudasaka, S. Iijima, N. Tagmatarchis** .... 5927 – 5933

Polymer Covalent Functionalization of Carbon Nanohorns Using Bulk Free Radical Polymerization



Bull by the horns: The covalent functionalization of carbon nanohorns is achieved by in situ bulk free radical polymerization (see figure). The functionalized material is used as a template for the synthesis of gold nanoparticles.

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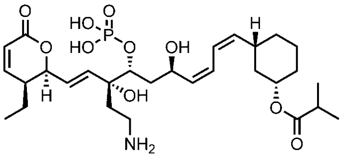
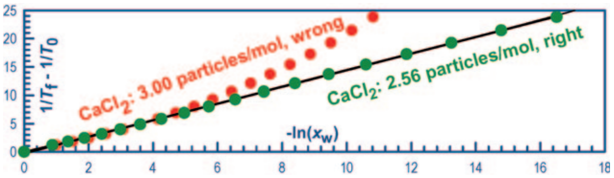
Perfect timing: The importance of the correct order of functional group introduction and manipulation (timing) was demonstrated in the course of a total synthesis of phoslactomycin A.



phoslactomycin A

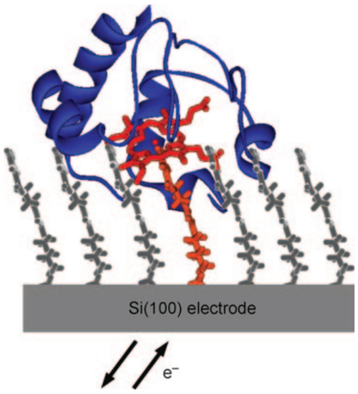
Natural Products



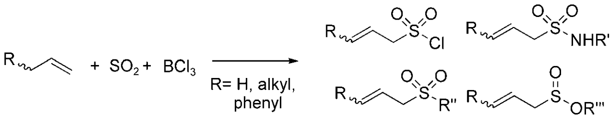
Ideal behavior: Contrary to widely held beliefs, many concentrated aqueous solutions of electrolytes and nonelectrolytes behave ideally (see graph). Hydration of solutes, ion pairing, solventbergs of amphiphiles, Hofmeister effects, ion-selective channels, ionic conductivities, viscosities, and so on, are all related to insights obtained from freezing-point depressions.

Water Chemistry

Bioelectronic devices: Pyridine-terminated monolayers were used to achieve the direct electron transfer with cytochrome c to give the first redox-protein-based bioelectronic device prepared on non-oxidized Si(100) electrodes (see figure). Electrodes presenting the putative heme ligand were prepared by a step-wise procedure using “click” reactions of acetylene-terminated alkyl monolayers and isonicotinic acid azide derivatives.



Bioelectrochemistry



For the first time, ene reactions of SO_2 with unfunctionalized alkenes are described (see scheme). As predicted by calculations, boron trihalides form stable complexes with sulfinic acids. These were used to generate β,γ-unsaturated sulfinyl and sulfonyl compounds. The one-pot, three-component synthesis of β,γ-unsaturated sulfonamides, sulfinyl esters, and sulfones has been developed starting from alkenes and sulfur dioxide.

C−H Activation

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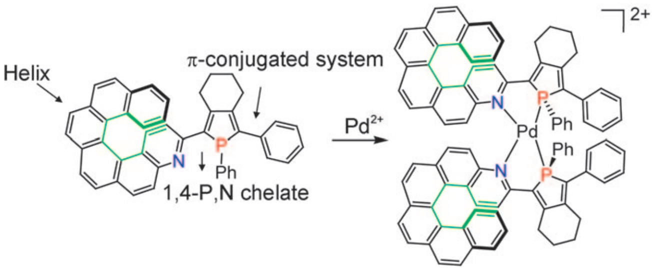
Chiral Azahelicene Phospholes

S. Graule, M. Rudolph, W. Shen,
J. A. G. Williams, C. Lescop,
J. Autschbach, J. Crassous,**
*R. Réau** . . . . 5976 – 6005

Assembly of π-Conjugated Phosphole Azahelicene Derivatives into Chiral Coordination Complexes: An Experimental and Theoretical Study

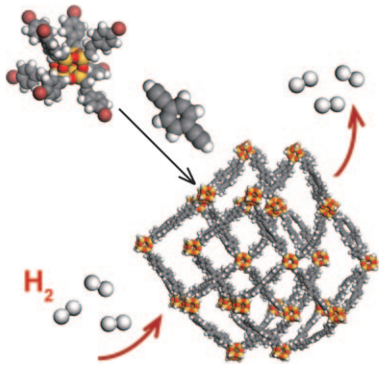


Chiral metal bis(helicene) complexes were obtained by stereoselective coordination of a new family of aza[*n*]helicene derivatives bearing a phosphole moiety to transition-metal centers (see scheme). The role played by the metal centers in tuning the chiroptical properties of these chiral π-conjugated assemblies is demonstrated and discussed on the basis of theoretical calculations.

Microporous Materials

W. Chaikittisilp, A. Sugawara,
*A. Shimojima, T. Okubo** . . 6006 – 6014

Hybrid Porous Materials with High Surface Area Derived from Bromophenylethenyl-Functionalized Cubic Siloxane-Based Building Units

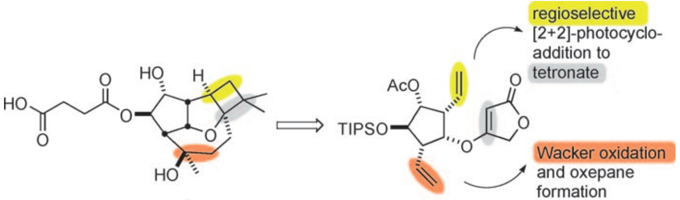


Linking the cubes! Porous inorganic–organic hybrids synthesized by cross-coupling of bromophenylethenyl-terminated cubic Si_8O_{12} siloxane cages with ethynyl compounds (see picture) have relatively high surface area and thermal stability. Moreover, they show high hydrogen uptakes with initial isosteric heats of hydrogen adsorption as high as 8.0 kJ mol^{-1}.

Natural Products

*M. Fleck, T. Bach** . . . . 6015 – 6032

Total Synthesis of Punctaporonin C by a Regio- and Stereoselective [2+2]-Photocycloaddition



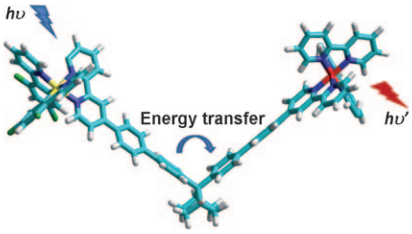
2

Both vinyl groups of tetronate **2** were incorporated into the structure of the unusual sesquiterpene natural product punctaporonin C (**1**). One double bond was involved in a regio- and diastereoselective tetronate [2+2]-photocycloaddition, the other double bond served as precursor for a methyl ketone, which underwent aldol ring-closure to the bridging oxepane.

Energy Transfer

J. Osío Barcina, N. Herrero-García,*
F. Cucinotta, L. De Cola,
P. Contreras-Carballada,
*R. M. Williams,**
*A. Guerrero-Martínez** . . . . . 6033 – 6040

Efficient Photoinduced Energy Transfer Mediated by Aromatic Homoconjugated Bridges



A bridge too far? Not only π or σ bridges, but also subunits with homoconjugated character, can be used as energy mediators in donor–bridge–acceptor systems. Bridges derived from cofacial 7,7-diphenylnorbornane mediate efficient energy transfer from the iridium(III) to the ruthenium(II) centres by a Dexter-type mechanism (see figure).

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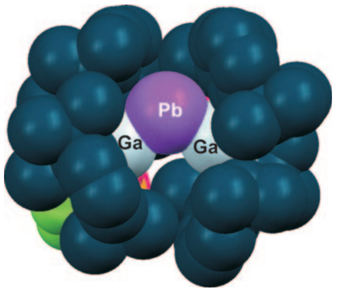
Lucky number 13: Oxidative addition of low-valent Group 13 metalloid N-heterocyclic carbene analogues of Ga^I–β-diketiminate with lead(II)/(IV) salts afforded the first structurally characterized monomeric molecular lead complexes (see image). Molecules of these types have not been reported until now.



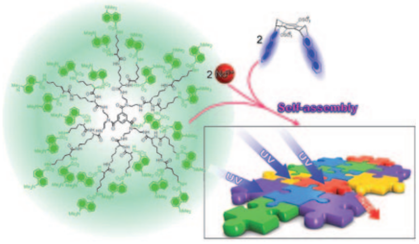
Oxidative Addition

*G. Prabusankar, C. Gemel, M. Winter, R. W. Seidel, R. A. Fischer** .... 6041 – 6047

Group 13 Ligand Supported Heavy-Metal Complexes: First Structural Evidence for Gallium–Lead and Gallium–Mercury Bonds

---

Molecular luminescent puzzle: Self-assembly of a dansylated dendrimer and two molecular clips with anthracene sidewalls is driven by two Nd^{3+} ions. The resulting architecture is a light-harvesting antenna that collects UV light and emits in the NIR spectral region (see graphic).



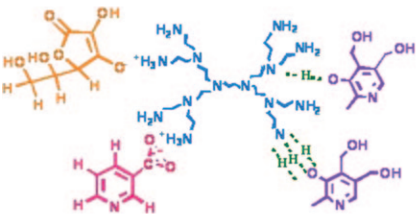
Self-Assembly

B. Branchi, P. Ceroni, V. Balzani, F.-G. Klärner, F. Vögtle* ..... 6048 – 6055

A Light-Harvesting Antenna Resulting from the Self-Assembly of Five Luminescent Components: A Dendrimer, Two Clips, and Two Lanthanide Ions

---

Vitamin capsules: Diaminobutane and polyamidoamine dendrimers interact with and encapsulate vitamins C, B_3, and B_6 in water (see scheme), as shown by ^1H NMR spectroscopic titrations in D_2O.



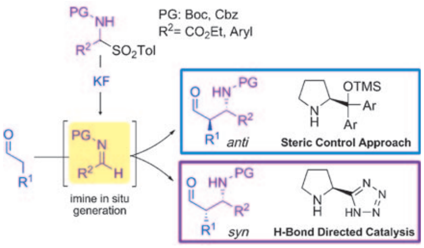
Dendrimers

*E. Boisselier, L. Liang, M. Dalko-Csiba, J. Ruiz, D. Astruc** .... 6056 – 6068

Interactions and Encapsulation of Vitamins C, B_3, and B_6 with Dendrimers in Water

---

Simple Mannich: In situ generation of highly reactive N-carbamate-protected imines from stable and easily handled α-amido sulfones accounts for the design of a very simple and highly efficient aminocatalytic Mannich strategy. The judicious selection of commercially available chiral amine catalysts allows full control of the stereochemistry of the Mannich process; both the *syn*- and *anti*-β-amino aldehydes are accessible with very high stereocontrol (see scheme).



Asymmetric Synthesis

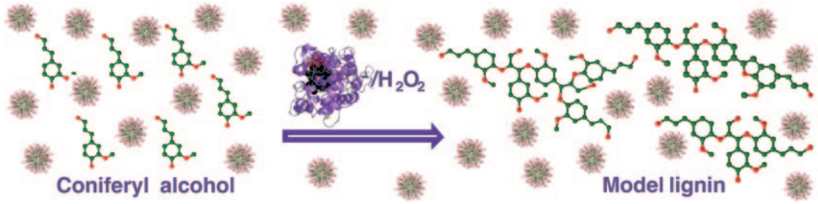
*P. Galzerano, D. Agostino, G. Bencivenni, L. Sambri, G. Bartoli, P. Melchiorre** .... 6069 – 6076

Controlling Stereoselectivity in the Aminocatalytic Enantioselective Mannich Reaction of Aldehydes with In Situ Generated N-Carbamoyl Imines

Biosynthetic Chemistry

*S. Reale, F. Attanasio, N. Spreti, F. De Angelis** .... 6077 – 6087

Lignin Chemistry: Biosynthetic Study and Structural Characterisation of Coniferyl Alcohol Oligomers Formed In Vitro in a Micellar Environment

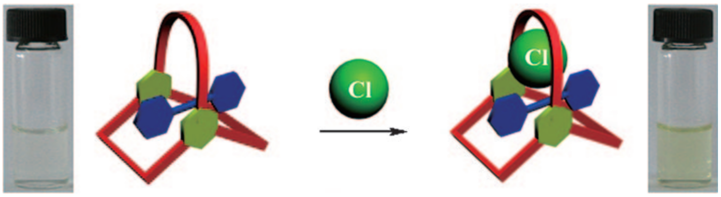


Mimicking nature: A model lignin was produced in a micellar medium that was able to keep all reaction products in solution (see figure). The reaction products were characterised by ^{1}H NMR spectroscopy and ESIMS. Ordered oligomer structures are obtained from a formal alternate sequence of a radical and an ionic step leading to a new biosynthetic perspective.

Host–Guest Systems

*K. Zhu, L. Wu, X. Yan, B. Zheng, M. Zhang, F. Huang** .... 6088 – 6098

Anion-Assisted Complexation of Paraquat by Cryptands Based on Bis(*m*-phenylene)-[32]crown-10

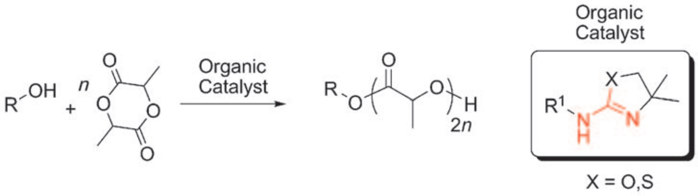


Ion-pair recognition: The complexation of tightly ion-paired divalent salts, such as paraquat dichloride, by cryptands based on crown ethers can be improved by the introduction of ion-pair recognition as a means of also binding the counteranions (see figure). This anion-assisted recognition motif has potential application for the development of anion-driven switchable molecular devices.

Organocatalysis

*J. M. Becker, S. Tempelaar, M. J. Stanford, R. J. Pounder, J. A. Covington, A. P. Dove** .... 6099 – 6105

Development of Amino–Oxazoline and Amino–Thiazoline Organic Catalysts for the Ring-Opening Polymerisation of Lactide

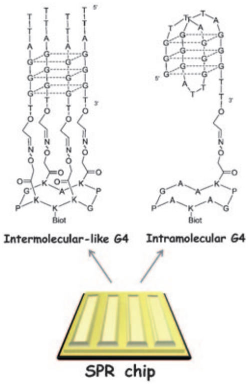


Organic catalysis: The ring-opening polymerisation of lactide by a range of amino–oxazoline and amino–thiazoline catalysts is reported (see scheme). The more electron-rich derivatives are demonstrated to be the most highly active and the polymerisation is well controlled. Investigations of the polymerisation mechanism are also reported.

DNA Ligation

*P. Murat, R. Bonnet, A. Van der Heyden, N. Spinelli, P. Labbé, D. Monchaud, M.-P. Teulade-Fichou, P. Dumy, E. Defrancq** .... 6106 – 6114

Template-Assembled Synthetic G-Quadruplex (TASQ): A Useful System for Investigating the Interactions of Ligands with Constrained Quadruplex Topologies



New biomolecular tool: A new biomolecular system for investigating the interactions of ligands with G-quadruplex conformations of DNA, using surface plasmon resonance (SPR), is described (see graphic). The method is based on the concept of template-assembled synthetic G-quadruplex (TASQ), which allows precise control of the parallel G-quadruplex conformation.

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💻 Supporting information on the WWW (see article for access details).

VIP Full Papers labeled with this symbol have been judged by two referees as being “very important papers”.

🎥 A video clip is available as Supporting Information on the WWW (see article for access details).

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CORRIGENDUM

D. A. Alonso, C. Nájera, I. M. Pastor,* M. Yus* 5274–5284

Transition-Metal-Catalyzed Synthesis of Hydroxylated Arenes

Chem. Eur. J., **2010**, *16*

DOI: 10.1002/chem.201000470

In the Minireview by Alonso, Pastor et. al., the wrong journal was cited in reference [18a], the correct reference is included below. We apologize for this oversight.
[18a] D. C. Powers, T. Ritter, *Nat. Chem.* **2009**, *1*, 302–309.

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