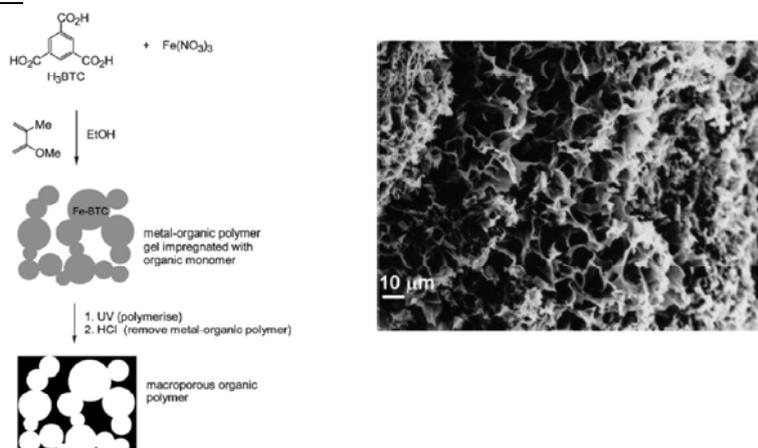


- Metal- and Anion-Binding Supramolecular Gels

Piepenbrock, M.-O. M.; Lloyd, G. O.; Clarke, N.; Steed, J. W. *Chem. Rev.* **2010**, *110*, 1960–2004.

1

Abstract:

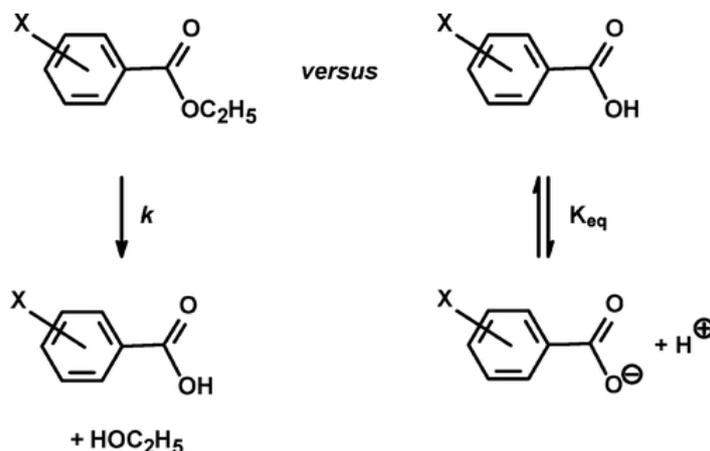


Gels are a commonplace household item and are easily identified by the simple “inversion test”; turn a pot of gel upside down and it is able to support its own weight without falling out onto your shoes! Examples such as hair gel, soft contact lenses, and “Jell-o” (or “Jelly” if you are English) all pass the inversion test and are instantly recognizable. These are all examples of *hydrogels*—two-component mixtures of a small amount (typically less than 2% by weight) usually of a polymer gelator immobilizing a much larger mass of water by surface tension effects.

- Reactivity Theory of Transition-Metal Surfaces: A Brønsted-Evans-Polanyi Linear Activation Energy-Free-Energy Analysis

Van Santen, R. A.; Neurock, M.; Shetty, S. G. *Chem. Rev.* **2010**, *110*, 2005–2048.

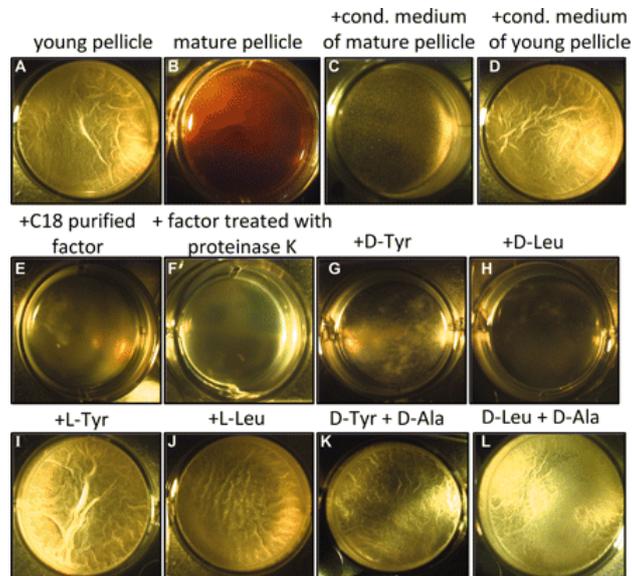
Abstract:



The exponential increase in computational processor speed, the development of novel computational architectures, together with the tremendous advances in ab initio theoretical methods that have emerged over the past two decades have led to unprecedented advances in our ability to probe the fundamental chemistry that occurs on complex catalytic surfaces. In particular, advances in density functional theory (DFT) have made it possible to elucidate the elementary steps and mechanisms in surface-catalyzed processes that would be difficult to explore experimentally.

- D-Amino Acids Trigger Biofilm Disassembly
Kolodkin-Gal, I.; Romero, D.; Cao, S.; Clardy, J.; Kolter, R.; Losick, R. *Science* **2010**, *328*, 627 – 629.

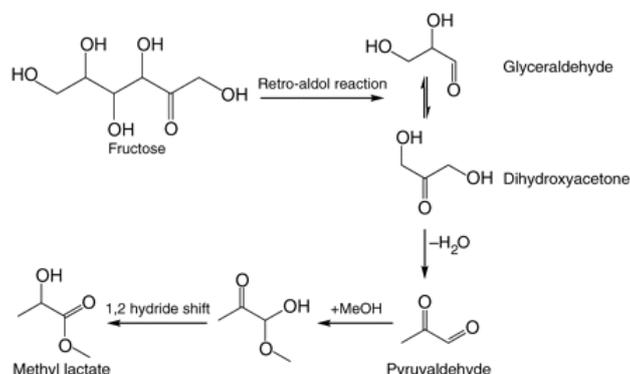
Abstract:



Bacteria form communities known as biofilms, which disassemble over time. In our studies outlined here, we found that, before biofilm disassembly, *Bacillus subtilis* produced a factor that prevented biofilm formation and could break down existing biofilms. The factor was shown to be a mixture of D-leucine, D-methionine, D-tyrosine, and D-tryptophan that could act at nanomolar concentrations. D-Amino acid treatment caused the release of amyloid fibers that linked cells in the biofilm together. Mutants able to form biofilms in the presence of D-Amino acids contained alterations in a protein (YqxM) required for the formation and anchoring of the fibers to the cell. D-Amino acids also prevented biofilm formation by *Staphylococcus aureus* and *Pseudomonas aeruginosa*. D-amino acids are produced by many bacteria and, thus, may be a widespread signal for biofilm disassembly.

- Conversion of Sugars to Lactic Acid Derivatives Using Heterogeneous Zeotype Catalysts
Spangenberg Holm, M.; Saravanamurugan, S.; Taarning, E. *Science* **2010**, *328*, 602 – 605.

Abstract:

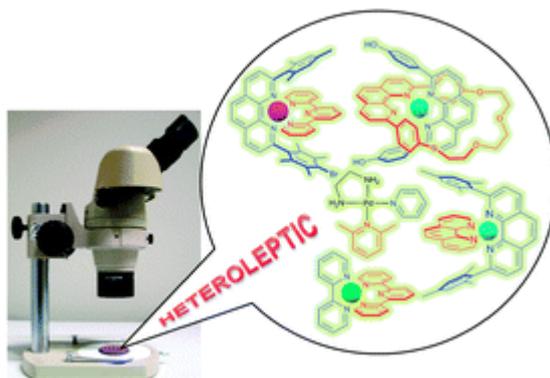


Presently, very few compounds of commercial interest are directly accessible from carbohydrates by using nonfermentive approaches. We describe here a catalytic process for

the direct formation of methyl lactate from common sugars. Lewis acidic zeotypes, such as Sn-Beta, catalyze the conversion of mono- and disaccharides that are dissolved in methanol to methyl lactate at 160°C. With sucrose as the substrate, methyl lactate yield reaches 68%, and the heterogeneous catalyst can be easily recovered by filtration and reused multiple times after calcination without any substantial change in the product selectivity.

- Metal-coordination-driven dynamic heteroleptic architectures
De, S.; Mahata, K.; Schmittl, M. *Chem. Soc. Rev.* **2010**, *39*, 1555 – 1575.

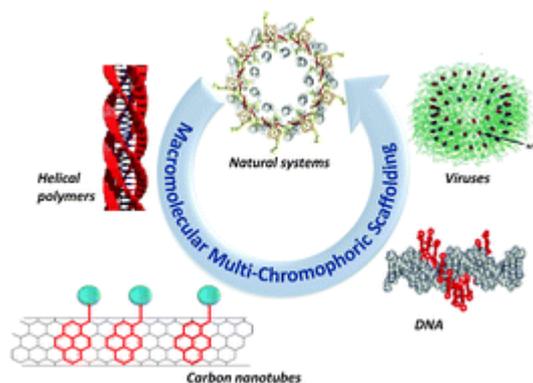
Abstract:



Dynamic heteroleptic coordination at metal centres is quite common in Nature and often related to a specific biological function, such as in zinc finger proteins and in hemoglobin for oxygen transport. To achieve the required high heteroleptic fidelity, representative biological systems avail themselves of “intramolecular” multidentate coordination using the protein backbone as a “superligand”. In contrast, dynamic heteroleptic coordination at a single metal centre in solution requires to bind different freely exchanging ligands under thermodynamic control. In this *tutorial review* we present the emerging principles of how to assemble dissimilar ligands at dynamically exchanging metal centres, with a particular emphasis on using the precepts for the fabrication of heteroleptic supramolecular assemblies in solution.

- Macromolecular multi-chromophoric scaffolding
Schwartz, E.; Le Gac, S.; Cornelissen, J. J. L. M.; Nolte, R. J. M.; Rowan, A. E. *Chem. Soc. Rev.* **2010**, *39*, 1576 – 1599.

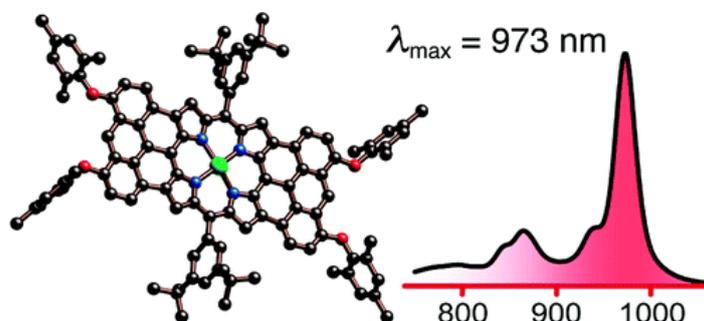
Abstract:



This *critical review* describes recent efforts in the field of chromophoric scaffolding. The advances in this research area, with an emphasis on rigid scaffolds, for example, synthetic polymers, carbon nanotubes (CNTs), nucleic acids, and viruses, are presented (166 references).

- Bis-AnthraceneFusedPorphyrins: Synthesis, Crystal Structure, and Near-IR Absorption
Davis, N. K. S.; Thompson, A. L.; Anderson, H. L. *Org. Lett.* **2010**, *12*, 2124–2127.

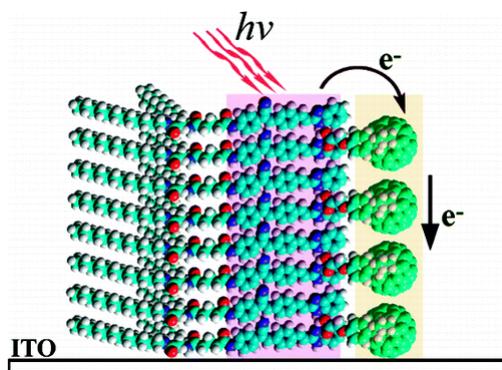
Abstract:



Synthesis of fused bis-anthraceneporphyrinmonomers and dimers has been achieved by oxidative ring closure using FeCl_3 and $\text{Sc}(\text{OTf})_3/\text{DDQ}$, respectively. The fused compounds display red-shifted absorption spectra with maxima in the near-IR at 973 and 1495 nm, respectively, and small electrochemical HOMO–LUMO gaps. The crystal structure of the fully fused bis-anthraceneporphyrin shows that it has a regular planar π -system.

- Hybrid Self-Assembly of a π Gelator and Fullerene Derivative with Photoinduced Electron Transfer for Photocurrent Generation
Xue, P.; Lu, R.; Zhao, L.; Xu, D.; Zhang, X.; Li, K.; Song, Z.; Yang, X.; Takafuji, M.; Ihara, H. *Langmuir* **2010**, *26*, 6669–6675.

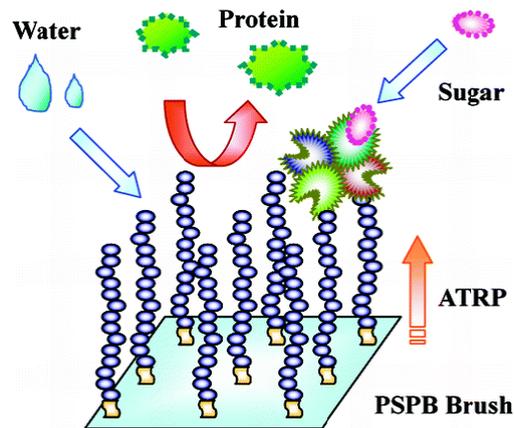
Abstract:



A π -conjugated organogelator (1) was synthesized, and its gelation ability was checked. It was found that it is an excellent gelator for some organic solvents, such as dichloromethane, benzene, o-dichlorobenzene, and DMSO/water. It can self-assemble into 1-D nanofibers induced by hydrogen bonding and π - π interactions. Moreover, 1 could form a hybrid gel with C_{60}COOH by hydrogen bonds in which 1 and C_{60}COOH can act as an electron donor and acceptor, respectively. It was found that the active film from the hybrid 1-D self-assemblies of 1 and C_{60}COOH showed remarkably higher photocurrent generation compared with that containing 1 and C_{60} because of the construction of interdigitated and ordered assemblies of donors and acceptors.

- Molecular Recognition at the Exterior Surface of a Zwitterionic Telomer Brush
Kitano, H.; Suzuki, H.; Matsuura, K.; Ohno, K. *Langmuir* **2010**, *26*, 6767–6774.

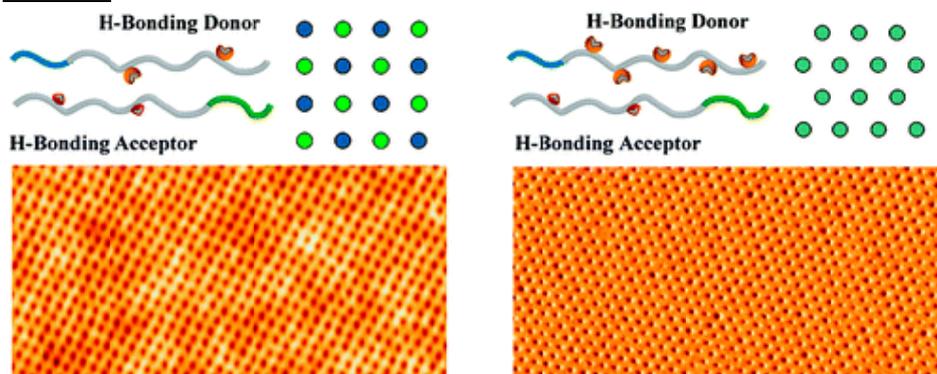
Abstract:



3-Sulfo-N,N-dimethyl-N-(20-methacryloyloxyethyl)propanaminium inner salt (SPB) was polymerized on a glass plate with a surface-confined initiator of atom transfer radical polymerization (ATRP) having a 2-bromoisobutyryl group. The glass plate modified with a brush of sulfobetaine telomer (PSPB) was highly hydrophilic and showed a strong resistance against nonspecific adsorption of proteins such as lysozyme and albumin. Through the polymerization from the free surface of PSPB chain by ATRP, furthermore, N-methacryloyloxysuccinimide (MAOSu) residues were introduced, and the incubation of the telomer (PSPB-b-PMAOSu)-modified glass chip with a lectin (concanavalin A, Con A) gave a glass chip covered with the Con-A-modified PSPB brush. The Con A fixed to the zwitterionic telomer brush pursued specific binding of mannose residues accumulated on the surface of Au colloidal particles, resulting in the increase in absorbance at 550 nm ascribable to localized surface plasmon resonance, while the nonspecific adsorption of proteins to the surface of the glass chip was still largely suppressed. The present results indicate usefulness of the zwitterionic telomer surface with antibiofouling properties as a scaffold for specific sensing devices.

- Thin Film Morphology of Block Copolymer Blends with Tunable Supramolecular Interactions for Lithographic Applications
Tang, C.; Hur, S.; Stahl, B. C.; Sivanandan, K.; Dimitriou, M.; Pressly, E.; Fredrickson, G. H.; Kramer, E. J. Hawker, C. J. *Macromolecules* **2010**, *43*, 2880–2889.

Abstract:



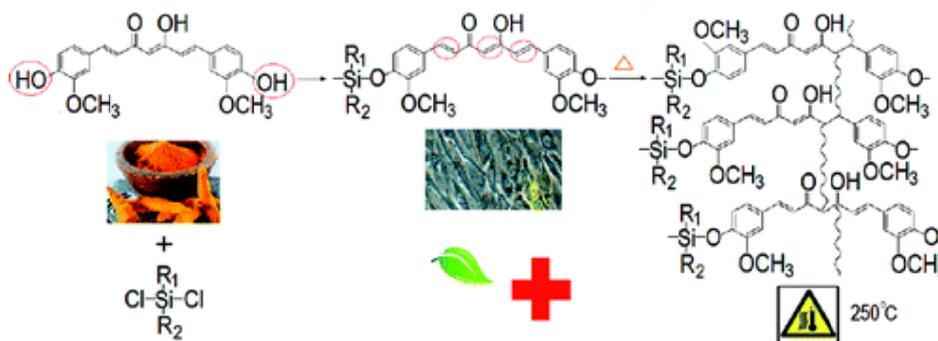
A modular and hierarchical self-assembly strategy using block copolymer blends (AB/B'C) with tunable supramolecular interactions is reported. By combining supramolecular assembly of hydrogen-bonding units with controlled phase separation of diblock copolymers, highly ordered square arrays or hexagonal arrays of cylindrical domains were obtained for mixtures

of poly(ethylene oxide)-*b*-poly(styrene-*r*-4-hydroxystyrene) (PEO-*b*-P(S-*r*-4HS)) and poly(styrene-*r*-4-vinylpyridine)-*b*-poly(methyl methacrylate) (P(S-*r*-4VP)-*b*-PMMA) diblock copolymers under solvent annealing with controlled high humidity. The fraction of the H-bonded phenolic and pyridyl units was shown to be critical for both the generation of long-range order and controlling the spatial arrangement of the cylindrical domains. Both low absolute numbers and a near-stoichiometric ratio of pyridyl-to-phenolic groups are needed to produce ordered square arrays with separated PEO and PMMA domains, whereas a low ratio of pyridyl-to-phenolic groups facilitated the formation of ordered hexagonal arrays with mixed PEO and PMMA domains. Self-consistent field theory simulations suggest that the effective Flory–Huggins parameters between the various blocks control the stability of the different packing structures in this system. The modularity and tunability of this supramolecular block copolymer blending approach is a unique and powerful strategy to fabricate diverse nanostructures for a variety of applications such as block copolymer lithography.

- Novel Thermally Cross-Linkable Poly[(arylenedioxy)(diorganylsilylene)]s Based on Curcumin: Synthesis and Characterization

Mukherjee, I.; Drake, K.; Berke-Schlessel, D.; Lelkes, P. I.; Yeh, J.-M.; Wie, Y. *Macromolecules* **2010**, *43*, 3277–3285.

Abstract:



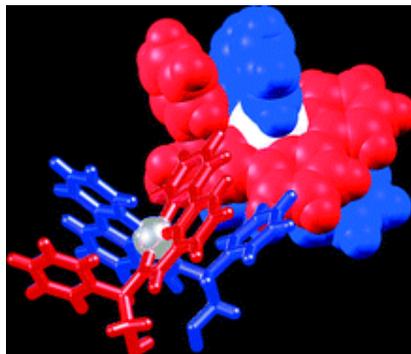
Curcumin has attracted much attention due to its chemopreventive and anti-inflammatory properties. Here we describe the synthesis of poly[(arylenedioxy)(diorganylsilylene)]s via polycondensation between curcumin and various diorganodichlorosilanes. These novel polymers incorporate the β -diketone unit of curcumin as well as the Si–O bond in the backbone. The polymer structure was characterized by means of ¹HNMR, FTIR, and elemental analysis, while GPC results showed high molecular weights. Preliminary cell culture results suggest lack of cytotoxicity, which is important for potential applications such as implant and scaffold materials. The T_g s of these polymers are in the 24 to 131 °C range, tunable by altering the pendant organic groups. The un-cross-linked polymers are stable at 250 °C in air. The presence of vinyl groups in the backbone also allows the possibility for thermal cross-linking. DSC and rheology data demonstrate that the materials can cross-link at a temperature above 200 °C which suggests the feasibility of melt processing these polymers via a technique wherein a low viscosity polymer is made to flow into a heated mold where it cross-links over time and becomes a rigid thermoset material.

- Π -Stacking and hydrogen bonding direct diastereoselectivity in one-pot syntheses of octahedral iron(II) complexes

Constable, E. C.; Zhang, G.; Housecroft, C. E.; Neuburger, M.; Zampese, J. A. *Chem. Commun.* **2010**, 46, 3077 – 3079.

7

Abstract:

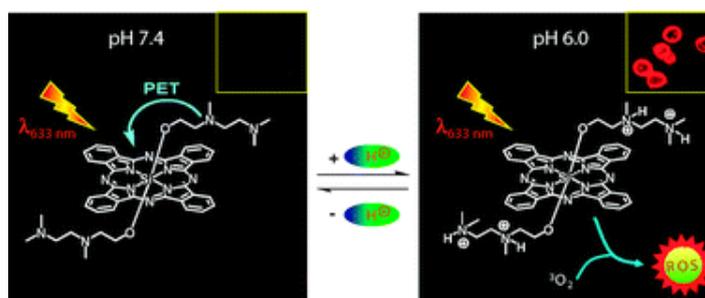


One-pot reactions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 2,2-bipyridine-6-carbaldehyde with enantiopure chiral amines lead to octahedral $[\text{FeL}_2]^{2+}$ complexes, the diastereoselectivity of which depends on the nature of the amine; an interplay of intra-cation π -stacking and hydrogen bonding directs the diastereoselectivity.

- A pH-responsive fluorescence probe and photosensitiser based on a tetraamino silicon(IV) phthalocyanine

Jiang, X. J.; Lo, P. C.; Yeung, S. L.; Fong, W. P.; Ng, D. K. P. *Chem. Commun.* **2010**, 46, 3188 – 3190.

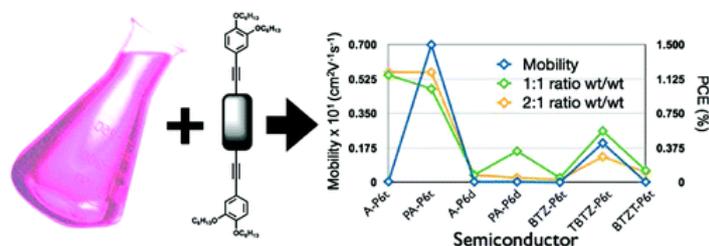
Abstract:



A novel tetraamino silicon(IV) phthalocyanine has been prepared, of which the fluorescence emission and reactive oxygen species generation efficiency are greatly enhanced at lower pH in the range of ca. 5–7, making it a promising pH-controlled and tumour-selective fluorescence probe and photosensitiser for photodynamic therapy.

- Solution-Processable Low-Molecular Weight Extended Arylacetylenes: Versatile p-Type Semiconductors for Field-Effect Transistors and Bulk Heterojunction Solar Cells

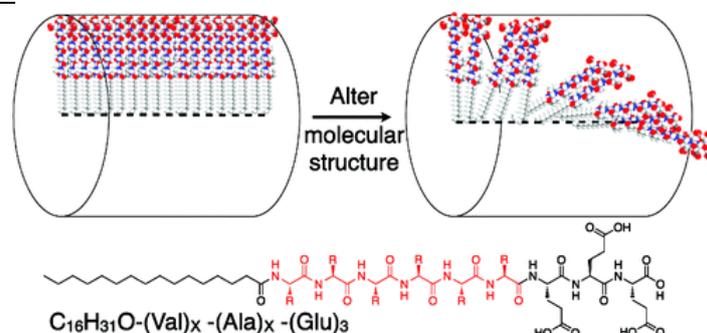
Abstract:



We report the synthesis and characterization of a series of five extended arylacetylenes, 9,10-bis-([m,p-bis(hexyloxy)phenyl]ethynyl)-anthracene (A-P6t, 1), 9,10-bis-[(p-([m,p-bis(hexyloxy)phenyl]ethynyl)phenyl)ethynyl]-anthracene (PA-P6t, 2), 4,7-bis-([m,p-bis(hexyloxy)phenyl]ethynyl)-2,1,3-benzothiadiazole (BTZ-P6t, 5), 4,7-bis(5-([m,p-bis(hexyloxy)phenyl]ethynyl)thien-2-yl)-2,1,3-benzothiadiazole (TBTZ-P6t, 6), and 7,7'-([m,p-bis(hexyloxy)phenyl]ethynyl)-2,1,3-benzothiadiazol-4,4'-ethynyl)-2,5-thiophene (BTZT-P6t, 7), and two arylvinylenes, 9,10-bis-[(E)-([m,p-bis(hexyloxy)phenyl]vinyl)-anthracene (A-P6d, 3), 9,10-bis-[(E)-(p-([m,p-bis(hexyloxy)phenyl]vinyl)phenyl)vinyl]-anthracene (PA-P6d, 4). Trends in optical absorption spectra and electrochemical redox processes are first described. Next, the thin-film microstructures and morphologies of films deposited from solution under various conditions are investigated, and organic field-effect transistors (OFETs) and bulk heterojunction photovoltaic (OPV) cells fabricated. We find that substituting acetylenic for olefinic linkers on the molecular cores significantly enhances device performance. OFET measurements reveal that all seven of the semiconductors are FET-active and, depending on the backbone architecture, the arylacetylenes exhibit good p-type mobilities (μ up to $\sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) when optimum film microstructural order is achieved. OPV cells using [6,6]-phenyl C_{61} -butyric acid methyl ester (PCBM) as the electron acceptor exhibit power conversion efficiencies (PCEs) up to 1.3% under a simulated AM 1.5 solar irradiation of 100 mW/cm^2 . These results demonstrate that arylacetylenes are promising hole-transport materials for p-channel OFETs and promising donors for organic solar cells applications. A direct correlation between OFET arylacetylene hole mobility and OPV performance is identified and analyzed.

- Tuning Supramolecular Rigidity of Peptide Fibers through Molecular Structure
Pashuck, E. T.; Cui, H.; Stupp, S. I. *J. Am. Chem. Soc.* **2010**, *132*, 6041–6046.

Abstract:



We synthesized a series of peptide amphiphiles (PAs) with systematically modified amino acid sequences to control the mechanical properties of the nanofiber gels they form by self-assembly. By manipulating the number and position of valines and alanines in the peptide sequence, we found that valines increase the stiffness of the gel, while additional alanines decrease the mechanical properties. Vitreous ice cryo-transmission electron microscopy shows that all PA molecules investigated here form nanofibers 8–10 nm in diameter and several micrometers in length. We found through Fourier transform IR experiments a strong correlation between gel stiffness and hydrogen bond alignment along the long axis of the fiber. Molecules that form supramolecular structures with the highest mechanical stiffness were found by circular dichroism to self-assemble into β -sheets with the least amount of twisting and disorder, a result that is consistent with IR experiments. Molecular control of mechanical

stiffness in three-dimensional artificial peptide amphiphile matrices offers a chemical strategy to control biological phenomena such as stem cell differentiation and cell morphology.

- The Impact of the Size of Dynamic Combinatorial Libraries on the Detectability of Molecular Recognition Induced Amplification

Ludlow, R. F.; Otto, S. J. *Am. Chem. Soc.* **2010**, *132*, 5984–5986.

Abstract:

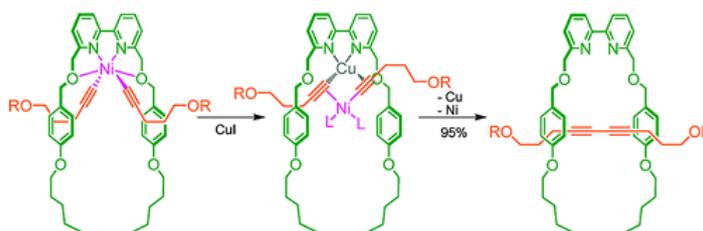


Despite well over a decade of research on dynamic combinatorial chemistry it is still unclear whether large libraries are more or less likely to yield strong binders than small libraries. We have now addressed this question by simulating a set of libraries containing from 65 to 4828 compounds under a range of different building block and template concentrations. We investigated the effect of library size on (i) the probability of detecting any amplification; (ii) the probability of detecting the strongest binding library member present; and (iii) the binding affinity of the most amplified detectable library member. The results indicate bigger libraries are more likely to produce better binders and that the affinity of the best binders identified rises more rapidly than expected statistically on the basis of the number of screened library members. This implies that it should be advantageous to work with DCLs that are much larger than the vast majority reported thus far.

- An Unusual Nickel–Copper-Mediated Alkyne Homocoupling Reaction for the Active-Template Synthesis of [2]Rotaxanes

Crowley, J. D.; Goldup, S. M.; Gowans, N. D.; Leigh, D. A.; Ronaldson, V. E.; Slawin, A. M. Z. *J. Am. Chem. Soc.* **2010**, *132*, 6243–6248.

Abstract:



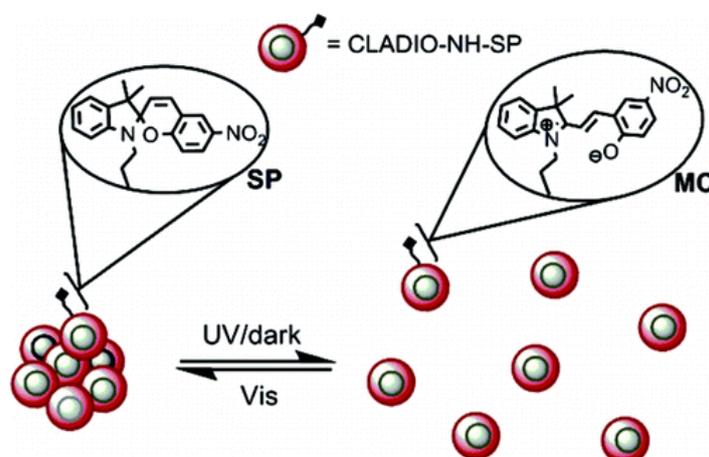
We report on an unusual Ni-/Cu-mediated alkyne homocoupling reaction, directed through the cavity of a bidentate macrocyclic ligand by chelated metal ions to furnish [2]rotaxanes in excellent (up to 95%) yields. This is the first active metal template reaction to employ an octahedral coordination geometry metal ion, Ni(II), and the study provides some interesting mechanistic insights into the mixed bimetallic reaction mechanism. The mixed-metal catalyst system was discovered serendipitously when Cu(I) was added to a Ni(II)-catalyzed alkyne homocoupling reaction in an attempt to facilitate chloride–acetylide ligand exchange. The role of Cu(I) in the reaction is, in fact, quite different from that originally intended. The effectiveness of having both nickel and copper present can be rationalized by the nature of a π -activated, σ -bonded, bimetallic intermediate in which the substitution of Ni(II) for one Cu(I)

ion in the classic bimetallic Glaser reaction mechanism apparently aids reductive elimination of the acetylide ligands. The system may prove useful for the development of general mixed-metal protocols for catalytic alkyne coupling reactions as well as being a highly effective route to rotaxanes with bis-acetylene threads, which are potentially useful for materials applications (insulated molecular wires) and in molecular machines (rigid, nonfolding axles).

- Modulation of T2 Relaxation Time by Light-Induced, Reversible Aggregation of Magnetic Nanoparticles

Osborne, E. A.; Jarrett, B. R.; Tu, C.; Louie, A. Y. *J. Am. Chem. Soc.* **2010**, *132*, 5934–5935.

Abstract:

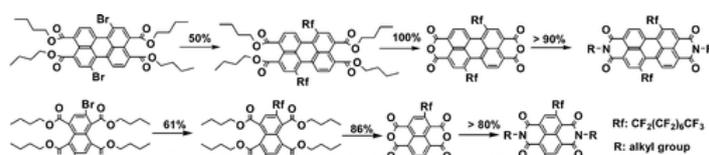


A reversible T2 contrast agent consisting of cross-linked anionic dextran coated iron oxide nanoparticles covalently coupled to a light-sensitive spiropyran (SP)/merocyanine (MC) motif was synthesized and characterized. In aqueous solution, light induced isomerization of the molecular switches between the hydrophobic SP isomer and hydrophilic MC isomer directs the aggregation and dispersion of the nanoparticles, respectively. When in the dark, where the MC form dominates, the probe has a T2 relaxation time of 37.09 ms (60 MHz, 37 °C) and two size populations at 70 and 540 nm. After irradiation with visible light, the T2 relaxation time is shortened 33.7%, and the size correspondingly shifts to a single population at 520 nm upon aggregation. This “smart” T2 agent provides the advantage of reversibility which may enable dynamic monitoring with MRI. In addition, the light responsiveness of this agent suggests the potential to employ them as MRI gene reporters for the luciferase expression system.

- Core-Perfluoroalkylated Perylene Diimides and Naphthalene Diimides: Versatile Synthesis, Solubility, Electrochemistry, and Optical Properties

Yuan, Z.; Li, J.; Xiao, Y.; Li, Z.; Qian, X. *J. Org. Chem.* **2010**, *75*, 3007–3016.

Abstract:



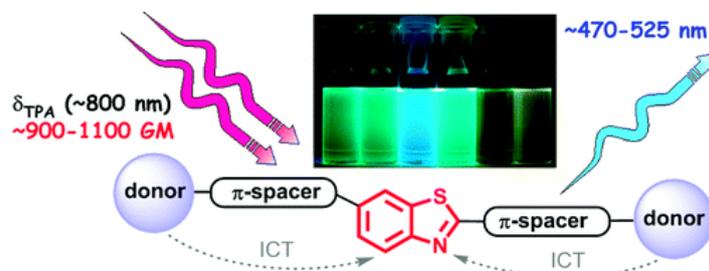
By a strategy featuring perfluoroalkylation of the highly soluble intermediates and their further efficient transformations to target compounds, a versatile synthesis of core-perfluoroalkylated perylene diimides (PDIs) and naphthalene diimides (NDIs) was developed, and PDIs

perfluoroalkylated at 1-position or 1,6-positions and core-perfluoroalkylated NDIs were first obtained. By esterification, perfluoroalkylation, hydrolysis, and condensation with amine, 1-perfluorooctyl-PDIs (**7b**, **7c**, and **7e**), 1,7-bis(perfluorooctyl)-PDIs (**8a–c** and **8e–g**), 1,6-bis(perfluorooctyl)-PDIs (**8'e**), a mixture of 1,7-bis(trifluoromethyl)-PDIs and 1,6-bis(trifluoromethyl)-PDIs (**11b** and **11'b**, **11d** and **11'd**, in a ratio of 19:1), 2-perfluorooctyl-NDIs (**20a–d**), and 2,6-bis(perfluorooctyl)-NDIs (**21a–21d**) were efficiently synthesized. Five valuable intermediates—1-perfluorooctylperylene dianhydride (**5**), 1,7-bis(perfluorooctyl)perylene dianhydride (**6**), 1,6-bis(perfluorooctyl)perylene dianhydride (**6'**), 2-perfluorooctyl-naphthalene dianhydride (**18**), and 2,6-bis(perfluorooctyl) naphthalene dianhydride (**19**)—were also obtained, and they can condense with many amines to produce PDIs containing different functional side chains on the imide nitrogen atoms. Solubility, electrochemistry, and optical properties of the above core-perfluoroalkylated PDIs and NDIs were investigated. Core-perfluoroalkylated **8e**, **8f**, **8'e**, mixture of **11d** and **11'd**, **20b**, and **20d** with excellent solubility in common organic solvents are competitive as candidates as solution processable semiconductors. Core-perfluoroalkylated PDIs and NDIs with experimental LUMO energy of 4.04–4.34 eV demonstrate strong electron accepting ability. For core-perfluoroalkylated PDIs, the maximum absorptions display blue shifts of 6–18 nm and the maximum molar extinction coefficients decrease obviously relative to those of unsubstituted PDIs, and they inherit the strong fluorescence from the PDIs family, which makes them promising fluorescent dyes.

- Benzothiazole-Based Fluorophores of Donor– π -Acceptor– π -Donor Type Displaying High Two-Photon Absorption

Hrobáriková, V.; Hrobárik, P.; Gajdo, P.; Fitisil, I.; Fakis, M.; Persephonis, P.; Zahradník, P. *J. Org. Chem.* **2010**, *75*, 3053–3068.

Abstract:



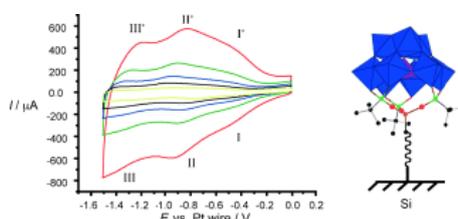
A series of novel heterocycle-based dyes with donor– π -bridge–acceptor– π -bridge–donor (D– π -A– π -D) structural motif, where benzothiazole serves as an electron-withdrawing core, have been designed and synthesized via palladium-catalyzed Sonogashira and Suzuki-type cross-coupling reactions. All the target chromophores show strong one-photon and two-photon excited emission. The maximum two-photon absorption (TPA) cross sections δ_{TPA} of the prepared derivatives bearing diphenylamino functionalities occur at wavelengths ranging from 760 to 800 nm and are as large as ~ 900 – 1100 GM. One- and two-photon absorption characteristics of the title dyes have also been investigated by using density functional theory (DFT) and the structure–property relationships are discussed. The TPA cross sections calculated by means of quadratic response time-dependent DFT using the Coulomb-attenuated CAM-B3LYP functional support the experimentally observed trends within the series, as well as higher δ_{TPA} values of the title compounds compared to those of analogous fluorene or carbazole-derived dyes. In contrast, the traditional B3LYP functional was not

successful in predicting the observed trend of TPA cross sections for systems with different central cores. In general, structural modification of the π -bridge composition by replacement of ethynylene (alkyne) with *E*-ethenylene (alkene) linkages and/or replacement of dialkylamino electron-donating edge substituents by diarylamino ones results in an increase of δ_{TPA} values. The combination of large TPA cross sections and high emission quantum yields makes the title benzothiazole-based dyes attractive for applications involving two-photon excited fluorescence (TPEF).

- Organosilyl/-germyl Polyoxotungstate Hybrids for Covalent Grafting onto Silicon Surfaces: Towards Molecular Memories

Joo, N.; Renaudineau, S.; Delapierre, G.; Bidan, G.; Chamoreau, L.-M.; Thouvenot, R.; Gouzerh, P.; Proust, A. *Chem. Eur. J.* **2010**, *16*, 5043-5051.

Abstract:

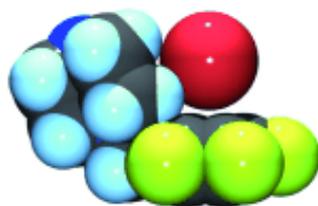


Organosilyl/-germyl polyoxotungstate hybrids $[\text{PW}_9\text{O}_{34}(\text{tBuSiO})_3\text{Ge}(\text{CH}_2)_2\text{CO}_2\text{H}]^{3-}$ (**1 a**), $[\text{PW}_9\text{O}_{34}(\text{tBuSiO})_3\text{Ge}(\text{CH}_2)_2\text{CONHCH}_2\text{C}\equiv\text{CH}]^{3-}$ (**2 a**), $[\text{PW}_{11}\text{O}_{39}\text{Ge}(\text{CH}_2)_2\text{CO}_2\text{H}]^{4-}$ (**3 a**), and $[\text{PW}_{11}\text{O}_{39}\text{Ge}(\text{CH}_2)_2\text{CONHCH}_2\text{C}\equiv\text{CH}]^{4-}$ (**4 a**) have been prepared as tetrabutylammonium salts and characterized in solution by multinuclear NMR spectroscopy. The crystal structure of $(\text{NBu}_4)_3\mathbf{1 a}\cdot\text{H}_2\text{O}$ has been determined and the electrochemical behavior of **1 a** and **2 a** has been investigated by cyclic voltammetry. Covalent grafting of **2 a** onto an n-type silicon wafer has been achieved and the electrochemical behavior of the grafted clusters has been investigated. This represents the first example of covalent grafting of Keggin-type clusters onto a Si surface and a step towards the realization of POM-based multilevel memory devices.

- CH-Directed Anion- π Interactions in the Crystals of Pentafluorobenzyl-Substituted Ammonium and Pyridinium Salts

Albrecht, M.; Müller, M.; Mergel, O.; Rissanen, K.; Valkonen, A. *Chem. Eur. J.* **2010**, *16*, 5062-5069.

Abstract:



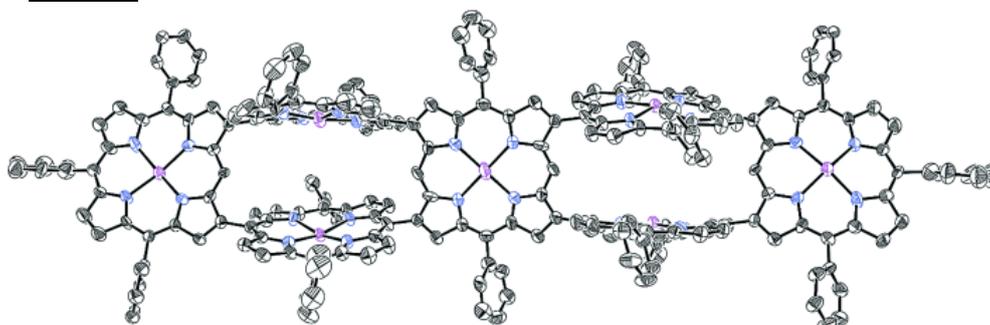
Simple pentafluorobenzyl-substituted ammonium and pyridinium salts with different anions can be easily obtained by treatment of the parent amine or pyridine with the respective pentafluorobenzyl halide. Hexafluorophosphate is introduced as the anion by salt metathesis. In the case of the ammonium salt **4**, water co-crystallisation seems to suppress effective anion- π interactions of bromide with the electron-deficient aromatic system, whereas with salts **5** and **6** such interactions are observed despite the presence of water. However, due to

asymmetric hydrogen-bonding interactions with ammonium side chains, the anion of **5** is located close to the rim of the pentafluorophenyl group (η^1 interaction). In **6** the CH-anion hydrogen bonding is more symmetric and fixes the anion on top of the ring (η^6). A similar structure-controlling effect is observed in case of the 1,4-diazabicyclo[2.2.2]octane derivatives **7**. Here the position of the anion (Cl, Br, I) is shifted according to the length of the weak CH-halide interaction. The hexafluorophosphate **7 d** reveals that this “non-coordinating” anion can be located on top of an aromatic π system. In the methyl-substituted pyridinium salts **9** and **10** different locations of the bromide anions with respect to the π system are observed. This is due to different conformations of the mono- versus disubstituted pyridine, which leads to different directions of the weak, but structurally important, $H_{Me}-Br$ bonds.

- Porphyrin Lego Block Strategy To Construct Directly meso- Doubly Linked Porphyrin Rings

Song, J.; Aratani, N.; Kim, P.; Kim, D.; Shinokubo, H.; Osuka, A. *Angew. Chem. Int. Ed.* **2010**, *49*, 3617-3620.

Abstract:

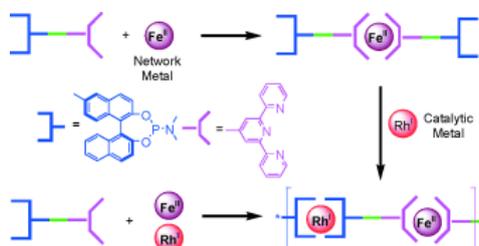


Clicking together: The Suzuki-Miyaura coupling of β,β' -diborylated porphyrin blocks and meso,meso'-dibrominated porphyrin blocks was used for the construction of directly meso- β doubly linked porphyrin rings including two tetraporphyrin rings, hexaporphyrin rings, and a bridged heptaporphyrin (see picture).

- Directed Orthogonal Self-Assembly of Homochiral Coordination Polymers for Heterogeneous Enantioselective Hydrogenation

Yu, L.; Wang, Z.; Wu, J.; Tu, S.; Ding, K. *Angew. Chem. Int. Ed.* **2010**, *49*, 3627-3630.

Abstract:



Three in one: Orthogonal coordination of Fe^{II} and Rh^I with a single heteroditopic ligand results in the formation of self-supported heterogeneous chiral catalysts (see scheme). The compounds are highly active, enantioselective, and reusable in the heterogeneous asymmetric hydrogenation of various functionalized olefin derivatives.