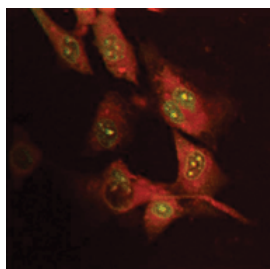


- Coordination and organometallic compounds as anion receptors and sensors  
Steed, J. W. *Chem. Soc. Rev.* **2009**, 38, 506 – 519.

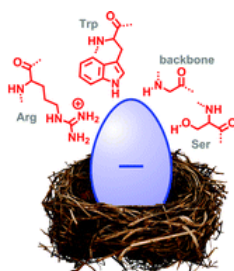
Abstract:



In this *tutorial review* the wide-ranging use of metal ions in anion receptors is discussed with an emphasis on diversity and applications in sensing and soft materials. Metal-containing receptors are categorised according to the role of the metal as a structural unit, as a Lewis-acidic binding site or as part of a redox-active or luminescent reporter group. The differing chemistry of substitutionally inert metal complexes in anion hosts and metal–anion–ligand self-assembly processes is highlighted. The use of anion binding coordination polymer systems in anion separations and in supramolecular gels is also examined.

- Amino acid containing anion receptors  
Kubik, S. *Chem. Soc. Rev.* **2009**, 38, 585 – 605.

Abstract:

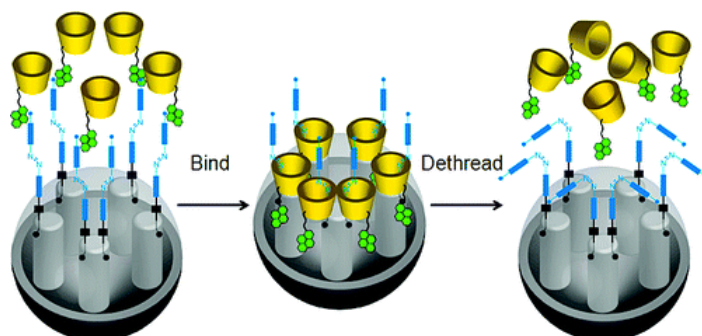


Nature has devised highly efficient and selective ways of recognizing anionic substrates by using surprisingly few building blocks the most important of which are the amino acids serine, tryptophane, and arginine in addition to NH groups along the protein backbone. Deliberate use of amino acids for the construction of abiotic anion receptors could lead to systems that mimic the anion coordinating properties of anion binding proteins. With this aim in mind several groups have focused their attention on the development of anion receptors containing amino acid building blocks and came up with remarkably efficient systems. This *critical review* summarizes the different approaches (174 references).

- Light-Operated Mechanized Nanoparticles

Ferris, D. J.; Zhao, Y.-L.; Khashab, N. M.; Khatib, H. A.; Stoddart, J. F.; Zink, J. I. *J. Am. Chem. Soc.* **2009**, *131*, 1686–1688.

Abstract:

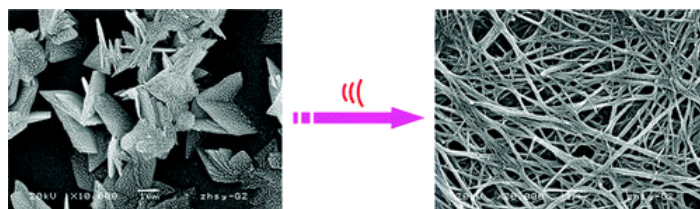


Mesoporous silica (MCM-41) nanoparticles modified by azobenzene derivatives, capable of storing small molecules and releasing them following light irradiation, have been fabricated and characterized. In the presence of the  $\beta$ -cyclodextrin and/or pyrene-modified  $\beta$ -cyclodextrin rings, the  $\beta$ -cyclodextrin and/or pyrene-modified  $\beta$ -cyclodextrin rings will thread onto the azobenzene-containing stalks and bind to *trans*-azobenzene units to form the pseudorotaxanes, thus sealing the nanopores and stopping release of the cargo. Upon irradiation, the isomerization of *trans*-to-*cis* azobenzene units leads to the dissociation of the  $\beta$ -cyclodextrin and/or pyrene-modified  $\beta$ -cyclodextrin rings from the stalks, thus opening the gates to the nanopores and releasing the cargo.

- Ultrasound-Induced Switching of Sheetlike Coordination Polymer Microparticles to Nanofibers Capable of Gelating Solvents

Zhang, S.; Yang, S.; Lan, J.; Tang, Y.; Xue, Y.; You, J. *J. Am. Chem. Soc.* **2009**, *131*, 1689–1691.

Abstract:

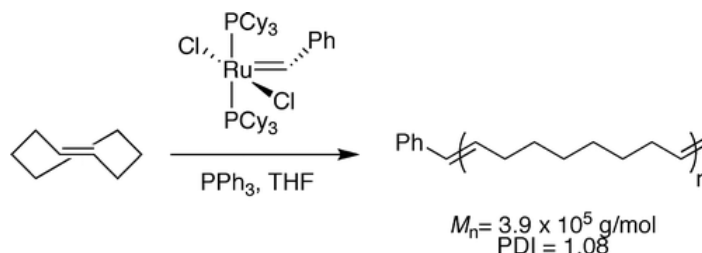


We herein demonstrate a new gelation mechanism based on a readily available coordination polymer  $\{Zn(bibp)_2(OSO_2CF_3)_2\}_n$ , in which ultrasound changes the morphology of the material from sheetlike microparticles into nanofibers, resulting in the immobilization of organic solvents.

- The Living ROMP of *trans*-Cyclooctene

Walker, R.; Conrad, R. M.; Grubbs, R. H. *Macromolecules* **2009**, *42*, 599-605.

Abstract :

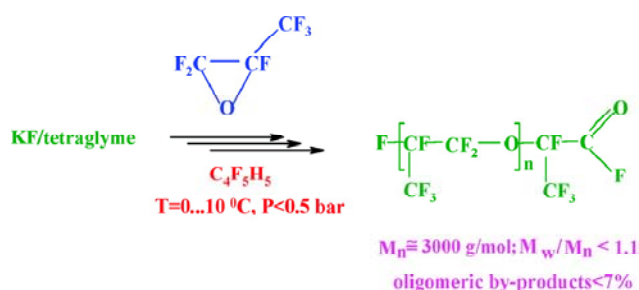


The living ring-opening metathesis polymerization (ROMP) of *trans*-cyclooctene (tCO) was investigated. ROMP of tCO in the presence of PPh<sub>3</sub> in THF leads to the formation of narrowly

dispersed polycyclooctene (PCO). The presence of PPh<sub>3</sub> as an additive and the use of THF as a solvent were demonstrated to be necessary to suppress competing secondary metathesis processes in the ROMP of tCO. Under optimal conditions, narrowly dispersed PCO was achieved without high molecular weight contaminants. The PCO was then hydrogenated to form linear, narrowly dispersed polyethylene with a melting temperature of 139 °C. Protected, hydroxy-functionalized tCO was polymerized by this method to afford narrowly dispersed, hydroxylated PCO. Block copolymers containing polynorbornene and PCO or containing differentially functionalized PCO were also synthesized and hydrogenated to form block copolymers containing blocks of linear, narrowly dispersed polyethylene.

- Anionic Ring-Opening Polymerization of Hexafluoropropylene Oxide Using Alkali Metal Fluorides as Catalysts: A Mechanistic Study  
Kostjuk, S. V.; Ortega, E.; Ganachaud, F.; Améduri, B.; Boutevin, B. *Macromolecules*, **2009**, *42*, 612-619.

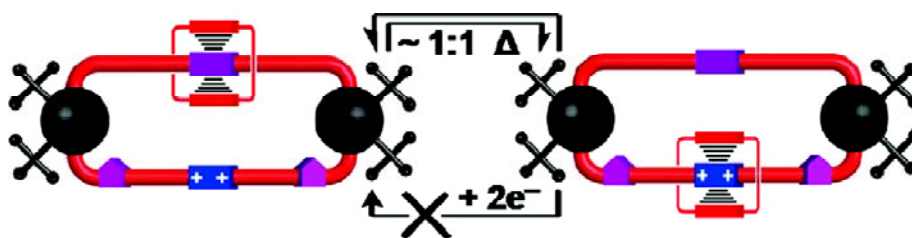
Abstract:



The anionic ring-opening polymerization of hexafluoropropylene oxide using the conventional alkali metal fluorides/tetraglyme catalytic system in the presence of different fluorinated solvents at various temperatures and under batch conditions is reported. Basically, the sodium fluoride (NaF)/tetraglyme system gave only monoadduct CF<sub>3</sub>CF<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>, while cesium fluoride (CsF)/tetraglyme produced oligomeric product with number-average degree of polymerization (DP<sub>n</sub>) less than 5. The higher molar mass polymers were synthesized using the potassium fluoride (KF)/tetraglyme catalytic system and 1,1,1,3,3-pentafluorobutane (C<sub>4</sub>F<sub>5</sub>H<sub>5</sub>) or 1,3-bis(trifluoromethyl)benzene as solvent at 0 °C. Under these conditions, polymers with number-average molar masses ranging between 2500 and 3500 g mol<sup>-1</sup> were obtained in high contents (>90%) and almost without any low molar mass (DP<sub>n</sub> ≤ 5) contaminants (4-7%). Polymers which chain ends were derived into methyl esters were fully characterized by gas chromatography, <sup>19</sup>F and <sup>1</sup>H NMR, and MALDI-TOF-MS spectroscopy. A kinetic study allowed us to propose a tentative mechanism entailing (i) the livingness of the polymerization of the hexafluoropropylene oxide with KF/tetraglyme catalytic system and (ii) the importance on the control of molar masses of the biphasic gas/liquid environment in the batch autoclave.

- A Reverse Donor-Acceptor Bistable [2]Catenane  
Coskun A.; Saha S.; Aprahamian I.; Stoddart J. F. *Org. Lett.*, **2008**, *10*, 3187-3190.

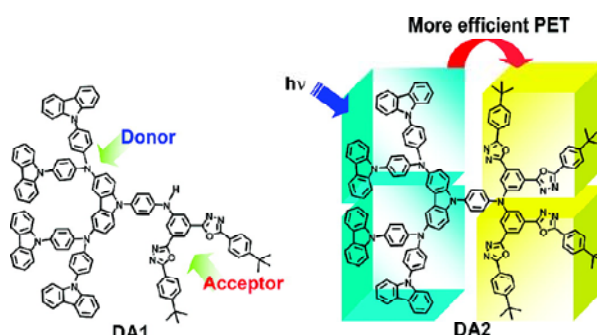
Abstract :



A [2]catenane, composed of a  $\pi$ -electron-rich bis-1,5-dioxynaphthalene[38]crown10 (BDNP38C10) ring, mechanically interlocked with a large macrocycle containing two disubstituted tetraarylmethane "speed bumps" and two different  $\pi$ -electron-deficient units—namely, naphthalene dimide (Npl) and bipyridinium ( $\text{BIPY}^{2+}$ ) units—has been synthesized from a [2]rotaxane, containing the former recognition unit, after performing two sequential Cu(I)-catalyzed azide-alkyne cycloadditions with a linker containing the latter recognition unit. The product, which exists as a single co-conformer, wherein the BDNP38C10 ring encircles the Npl unit, undergoes equilibration to give approximately equal amounts of the other co-conformer in which the BDNP38C10 ring encircles the  $\text{BIPY}^{2+}$  unit.

- Modulate Photoinduced Electron Transfer Efficiency of Bipolar Dendritic Systems  
Lin Y.-H.; Wu H.-H.; Wong K.-T.; Hsieh C.-C.; Lin Y.-C.; Chou P.-T. *Org. Lett.*, **2008**, 10, 3211-3214.

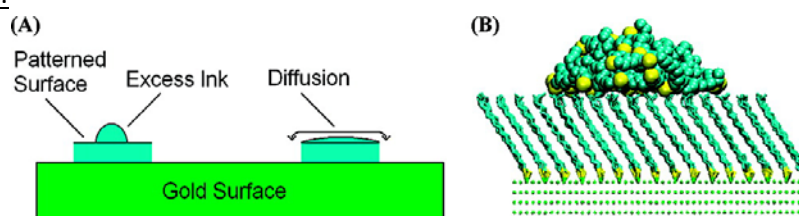
Abstract :



Covalent linkage of dendritic carbazole-based donors and 1,3,4-oxdiazole-based acceptors renders novel bipolar dendrimers that can efficiently facilitate the photoinduced electron transfer (PET) process. Photodynamic studies indicated that the PET rate of bipolar dendrimers DA1 and DA2 can be modulated by the number of acceptors presented in the molecule.

- Quantification of Ink Diffusion in Microcontact Printing with Self-Assembled Monolayers  
Gannon, G.; Larsson, J. A.; Greer, J. C.; Thompson, D. *Langmuir* **2009**, 25, 242-247.

Abstract:



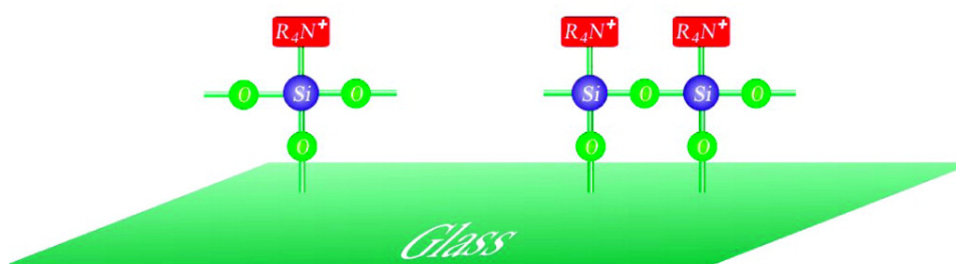
Spreading of ink outside the desired printed area is one of the major limitations of microcontact printing ( $\mu$ -CP) with alkanethiol self-assembled monolayers (SAMs) on gold. We use molecular dynamics (MD) computer simulations to quantify the temperature and concentration dependence of hexadecanethiol (HDT) ink spreading on HDT SAMs, modeling 18 distinct printing conditions using

periodic simulation cells of  $\sim 7$  nm edge length and printing conditions ranging from 7 ink molecules per cell at 270 K to 42 ink molecules per cell at 371 K. The computed alkanethiol ink diffusion rates on the SAM are of the same order of magnitude as bulk liquid alkanethiol diffusion rates at all but the lowest ink concentrations and highest temperatures, with up to 20-30 times increases in diffusion rates at the lowest concentration-highest temperature conditions. We show that although alkanethiol surfaces are autophobic, autophobicity is not enough to pin the ink solutions on the SAM, and so any overinking of the SAM will lead to spreading of the printed pattern. Comparison of experimental and calculated diffusion data supports an interpretation of pattern broadening as a mixture of spreading on fully and partially formed SAMs, and the calculated spreading rates establish some of the fundamental limitations of  $\mu$ -CP in terms of stamp contact time and desired pattern width.

- A Novel Application of Quaternary Ammonium Compounds as Antibacterial Hybrid Coating on Glass Surfaces

Saif, M. J.; Anwar, J.; Munawar, M. A. *Langmuir* **2009**, 25, 377-379.

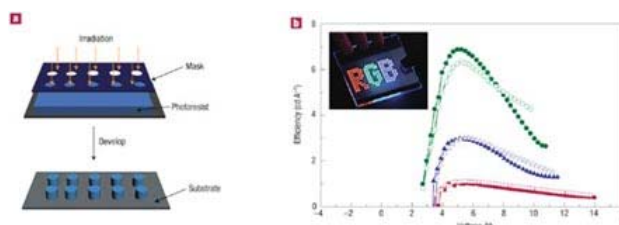
Abstract:



A hybrid coating is prepared on a glass surface by a sol-gel process using tetraethoxysilane (TEOS) and Q4N<sup>+</sup>-Si(OR)<sub>3</sub>. Transparent coatings with smooth surfaces were investigated against both Gram-positive (*Escherichia coli*) and Gram-negative bacteria (*Staphylococcus aureus*). A rapid decrease of the count for both strains was observed within 72 h. A significant correlation has been observed between the concentration of Q4N<sup>+</sup>-Si(OR)<sub>3</sub> and the antibacterial activity which has been thoroughly investigated.

- Patterning surfaces with functional polymers
- Nie, Z.; Kumacheva, E. *Nature Materials* **2008**, 7, 277-290.

Abstract:



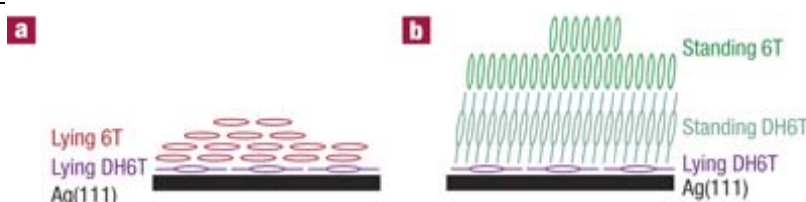
The ability to pattern functional polymers at different length scales is important for research fields including cell biology, tissue engineering and medicinal science and the development of optics and electronics. The interest and capabilities of polymer patterning have originated from the abundance of functionalities of polymers and a wide range of applications of the patterns. This paper reviews recent advances in top-down and bottom-up patterning of polymers using photolithography, printing

techniques, self-assembly of block copolymers and instability-induced patterning. Finally, challenges and future directions are discussed from the point of view of both applicability and strategies for the surface patterning of polymers.

- Orientation-dependent ionization energies and interface dipoles in ordered molecular assemblies

Duhm, S.; Heimel, G.; Salzmann, I.; Glowatzki, H.; Johnson, R. L.; Vollmer, A.; Rabe, J. P.; Koch, N. *Nature Materials* **2008**, 7, 326-332.

Abstract:

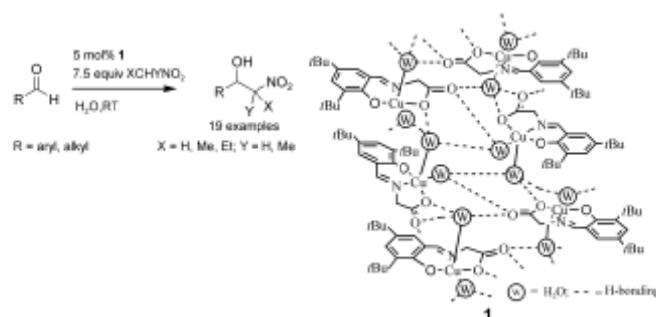


Although an isolated individual molecule clearly has only one ionization potential, multiple values are found for molecules in ordered assemblies. Photoelectron spectroscopy of archetypical  $\pi$ -conjugated organic compounds on metal substrates combined with first-principles calculations and electrostatic modelling reveal the existence of a surface dipole built into molecular layers. Conceptually different from the surface dipole at metal surfaces, its origin lies in details of the molecular electronic structure and its magnitude depends on the orientation of molecules relative to the surface of an ordered assembly. Suitable pre-patterning of substrates to induce specific molecular orientations in subsequently grown films thus permits adjusting the ionization potential of one molecular species over up to 0.6 eV via control over monolayer morphology. In addition to providing in-depth understanding of this phenomenon, our study offers design guidelines for improved organic–organic heterojunctions, hole- or electron-blocking layers and reduced barriers for charge-carrier injection in organic electronic devices.

- Synthesis, Structure, and Application of Self-Assembled Copper(II) Aqua Complex by H-Bonding for Acceleration of the Nitroaldol Reaction on Water

Jammi, S.; Ali, A.; Sakthivel, L.; Rout, L.; Punniyamurthy, T. *Chem. Asian J.* **2009**, 4, 314 – 320.

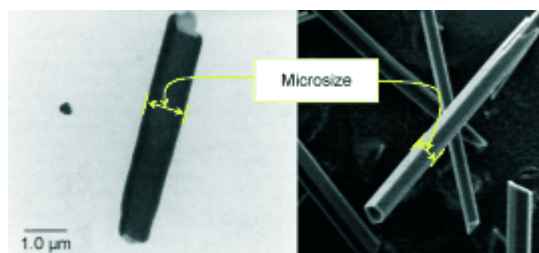
Abstract:



Copper(II) aqua complex 1 has been prepared in a one-pot synthesis. The single crystal X-ray analysis showed that the complex is self-assembled through aqua ligands by H-bond interactions and the copper(II) atoms are pentacoordinated with square pyramidal geometry. Complex 1 has been studied for the acceleration of the nitroaldol reaction on water. It is a clean technological process and the catalyst can be recycled without loss of activity.

- Self-Assembled Organic Microtubes from Amphiphilic Molecules  
Lee H. Y.; Nam, S. R.; and Hong J. *Chem. Asian J.* **2009**, 4, 226 – 235

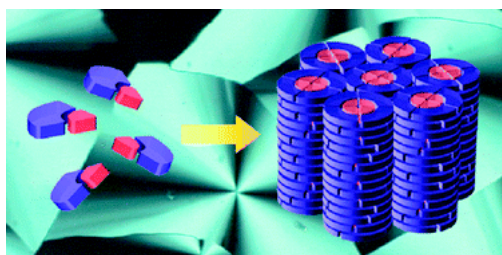
Abstract:



In recent years, there have been increasing numbers of reports about self-assembled nano- or microtubular structures, because they have potential uses in nanofabrication, purification, medical, and encapsulation applications. A wide range of tubular structures have been constructed by the self-assembly of amphiphilic molecules in aqueous solution or organic solvents. The diameters of self-assembled tubular structures range between 10 nm and 30 nm. One of the most important factors that determine their suitability for technical applications is the size of the tubes. Therefore, analyzing and sorting tubular structures according to their size is essential. This Focus Review highlights micro-sized self-assembled organic tubular structures formed in aqueous solutions and organic solvents.

- Self-assembly of functional columnar liquid crystals  
Kato, T.; Yasuda, T.; Kamikawa, Y.; Yoshio, M. *Chem. Commun.* **2009**, 729 – 739.

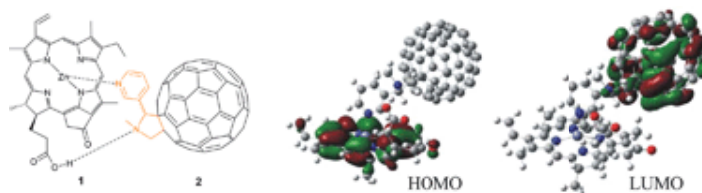
Abstract :



Columnar liquid crystals have recently been developed as dynamically functional anisotropic materials. In this feature article, some recent examples of the materials design and functionalisation of columnar liquid crystals are described. Not only disklike molecules but also molecules with unconventional shapes can form columnar liquid-crystalline assemblies with nanosegregated structures. Moreover use of non-covalent interactions such as hydrogen bonding, ionic and electron donor–acceptor interactions leads to the formation of supramolecular functional columnar materials that are stimuli-responsive. Nanosegregated columnar molecular order can also be used for one-dimensional transportation of electrons, ion and molecules.

- Zn pyro-pheophorbide a—fulleronicotinic dyad; supramolecular self assembled donor–acceptor system for photoinduced charge separation.  
Kavakka, J. S.; Heikkinen, S.; Kilpeläinen, I.; Tkachenko, N. V.; Helaja, J. *Chem. Commun.*, **2009**, 758 – 760.

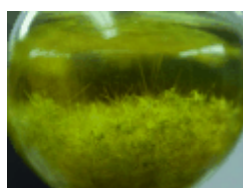
Abstract :



Zn pyro-pheophorbide a and fullerene form in nonpolar solvents a supramolecular self-assembled electron donor–acceptor dyad, which performs fast photoinduced charge separation (0.5 ps) and slow recombination (>1 ns) as evidenced by photochemical studies.

- Investigation of  $sp^2$ - $sp$  Coupling for Electron-Enriched Aryl Dihalides under Oxygen-Free Sonogashira Coupling Reaction Conditions Using a Two-Chamber Reaction System  
Chen, X.-Y.; Barnes, C. ; Dias, J. R.; Sandreczki, T. C. *Chem. Eur. J.* **2009**, *15*, 2041-2044.

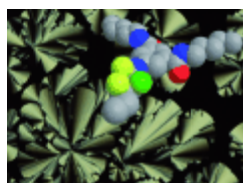
Abstract:



**Triethylamine hydroiodide crystals** were formed during Sonogashira reactions; after complete reaction the solution retains a characteristic light color (see picture). Very sluggish Sonogashira reactions of electron-enriched aryl diiodides have been carried out in high yield in an oxygen-free, two-chamber reaction system. The formation of triethylamine hydroiodide crystals was monitored to determine the completion of reaction.

- Asymmetrically Substituted Benzene-1,3,5-tricarboxamides: Self-Assembly and Odd-Even Effects in the Solid State and in Dilute Solution  
Stals, P. J. M.; Smulders, M. M. J.; Martín-Rapún, R.; Palmans, A. R. A.; Meijer, E. W. *Chem. Eur. J.* **2009**, *15*, 2071-2080.

Abstract:

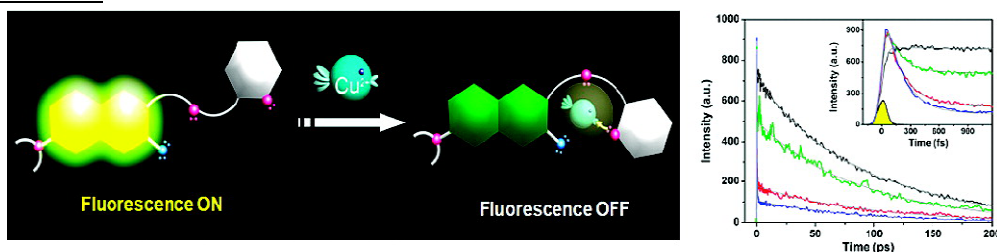


**Molecular organization:** Chiral benzene tricarboxamides with methyl substituents at defined positions self-assemble into supramolecular polymers of preferred helicity by three-fold  $\alpha$ -helical-type hydrogen bonding. The odd-even effect is operative and all derivatives are liquid crystalline showing a  $Col_{ho}$  phase (see figure). Asymmetric benzene-1,3,5-tricarboxamides (aBTAs) comprising two *n*-octyl and one chiral methyl-alkyl side chain were synthesised and characterised. The influence of the position and the configuration of the chiral methyl group (methyl at the  $\alpha$ ,  $\beta$  or  $\gamma$  position) in the aliphatic side chains on the liquid-crystalline properties and the aggregation behaviour of the aBTAs was systematically studied and compared to symmetrical benzene-1,3,5-tricarboxamides (sBTAs). Solid-state characterisation (polarised optical microscopy, IR spectroscopy, X-ray diffraction and differential scanning calorimetry) revealed that all aBTAs show threefold,  $\alpha$ -helical-type intermolecular hydrogen bonding between neighbouring molecules and exhibit a columnar hexagonal organisation from room temperature to well above 200 °C. Moving the chiral methyl

group closer to the amide group stabilises the liquid-crystalline state, as evidenced by a higher clearing temperature and corresponding enthalpy. The self-assembly of dilute solutions of the aBTAs in methylcyclohexane ( $\approx 10^{-5}$  mol L<sup>-1</sup>) was investigated with circular dichroism (CD) spectroscopy. The sign of the Cotton effect demonstrated a pronounced odd-even effect, whereas the value of the molar ellipticity,  $\Delta \epsilon$ , in the aBTAs was independent of the position of the methyl group. Subsequent temperature-dependent CD measurements showed that the aggregation of all aBTAs can quantitatively be described by the nucleation-growth model and that the stability of the aggregates increases when the chiral methyl group is closer to the amide moiety. The results presented herein illustrate that even small changes in the molecular structure of substituted benzene-1,3,5-tricarboxamides affect their solid-state properties and their self-assembly behaviour in dilute solutions.

- Coumarin-Derived Cu<sup>2+</sup>-Selective Fluorescence Sensor: Synthesis, Mechanisms, and Applications in Living Cells**  
 Jung, H. S.; Kwon, P. S.; Lee, J. W.; Kim, J.; Hong, C. S.; Kim, J. W.; Yan, S.; Lee, J. Y.; Lee, J. H.; Joo, T.; Kim, J.S. *J. Am. Chem. Soc.*, **2009**, *131*, 2008–2012.

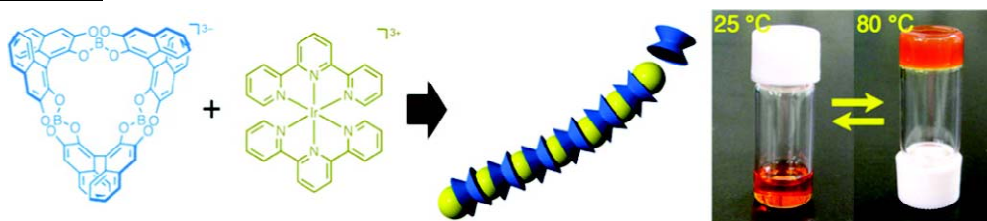
Abstract:



A novel coumarin-based fluorogenic probe bearing the 2-picolyl unit (**1**) was developed as a fluorescent chemosensor with high selectivity and suitable affinity in biological systems toward Cu<sup>2+</sup> over other cations tested. The fluorescence on-off mechanism was studied by femtosecond time-resolved fluorescence (TRF) upconversion technique and ab initio calculations. The receptor can be applied to the monitoring of Cu<sup>2+</sup> ion in aqueous solution with a pH span 4–10. To confirm the suitability of **1** for biological applications, we also employed it for the fluorescence detection of the changes of intracellular Cu<sup>2+</sup> in cultured cells. The results indicate that **1** should be useful for the fluorescence microscopic imaging and the study on the biological functions of Cu<sup>2+</sup>.

- Back to Back Twin Bowls of D<sub>3</sub>-Symmetric Tris(spiroborate)s for Supramolecular Chain Structures**  
 Danjo, H.; Hirata, K.; Yoshigai, S.; Azumaya, I.; Yamaguchi, K. *J. Am. Chem. Soc.*, **2009**, *131*, 1638–1639.

Abstract:



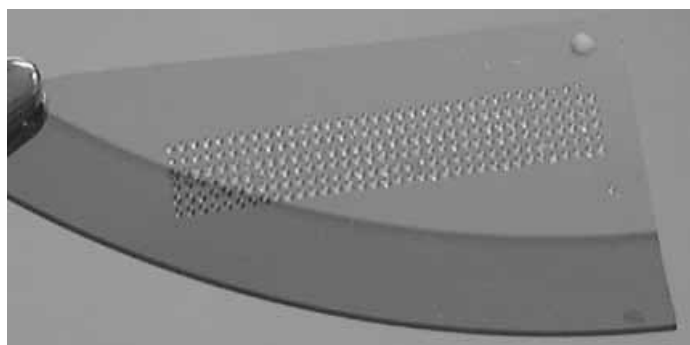
A new class of D<sub>3</sub>-symmetric tris(spiroborate) cyclophanes has been designed and prepared for the construction of supramolecular chain structures by iterative host–guest interaction with ditopic guest molecules. The treatment of these compounds with [Ir(tpy)<sub>2</sub>](PF<sub>6</sub>)<sub>3</sub> complex in solution led to the

formation of the chain structure, which was confirmed by  $^1\text{H}$  NMR and CSI-MS studies. The chain structure exhibited rapid temperature-responsive gelation behavior in their HMPA sol.

- Hydrogels for Soft Machines

Calvert, P. *Adv. Mater.* **2009**, *21*, 743-756.

Abstract :

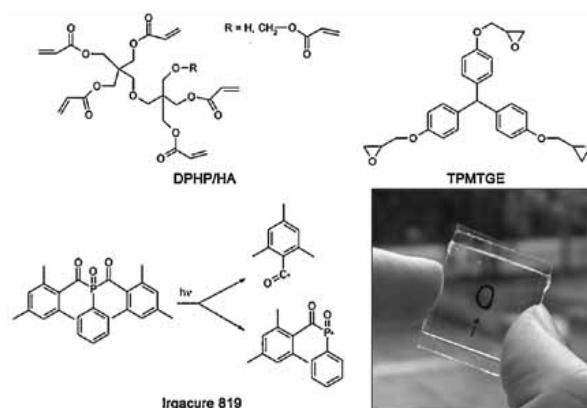


Until recently, synthetic gels have been too weak for any engineering use. Strong double-network gels and other reinforced gels open the possibility of new biomedical devices, and may replace rubber in some applications. Immediate needs include a better understanding of the relationship between mechanical properties and structure in gels, and convenient methods for processing gels.

- Superior-Performance Polymeric Composite Materials for High-Density Optical Data Storage

Castagna, R.; Vita, F.; Lucchetta, D. E.; Criante, L.; Simoni, F. *Adv. Mater.* **2009**, *21*, 589-592.

Abstract :

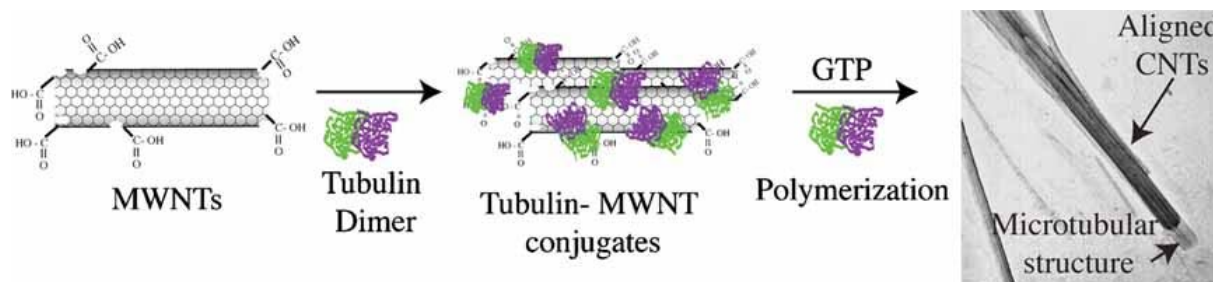


High-resolution holographic gratings are obtained using a combination of a multifunctional acrylate (DPHP/HA), a low-molecular-weight glass-forming liquid epoxy-aromatic resin (TPMTGE), and a UV-photoinitiator (Irgacure 819). Their optical properties (sensitivity, transparency, and optical shrinkage) are promising for high-density optical data storage applications.

- Tubulin Encapsulation of Carbon Nanotubes into Functional Hybrid Assemblies

Dinu, C. Z.; Bale, S. S.; Zhu, G.; Dordick, J. S. *Small* **2009**, *5*, 310-315.

Abstract:



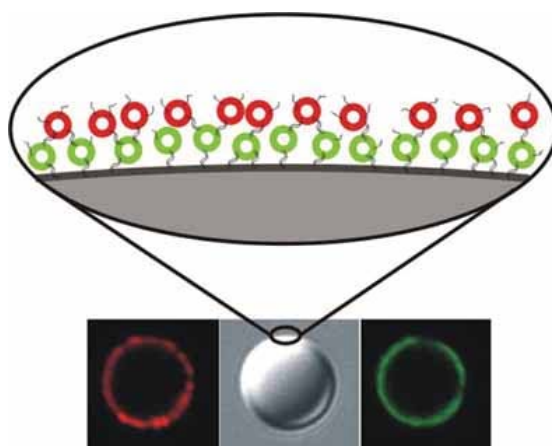
11

Functional multi-walled carbon nanotubes (MWNTs) are obtained by conjugation of MWNTs with tubulin. In vitro polymerization of tubulin-MWNT conjugates with excess free tubulin results in the microtubules encapsulating the MWNTs to yield nanotube-based biohybrids. The functional biohybrids are manipulated on kinesin-coated surfaces. This strategy represents a new paradigm for the design of hierarchical supramolecular assemblies.

- Controlled Assembly of Vesicle-Based Nanocontainers on Layer-by-Layer Particles via DNA Hybridization

Loew, M.; Kang, J.; Dähne, L.; Hendus-Altenburger, R.; Kaczmarek, O.; Liebscher, J.; Huster, D.; Ludwig, K.; Böttcher, C.; Herrmann, A.; Arbuzova, A. *Small* **2009**, 5, 320-323.

Abstract:



Microscopic colloidal particles allow a precise regulation of chemical reactions in time and place. A controlled assembly of multiple layers of intact lipid vesicles on a solid support provided by layer-by-layer particles functionalized by a covalent attachment of DNA oligonucleotides is reported (see image). Lipophilic complementary oligonucleotides are incorporated into lipid vesicles. Fusion of liposomes and release can be triggered.