1

 Length-Dependent Convergence and Saturation Behavior of Electrochemical, Linear Optical, Quadratic Nonlinear Optical, and Cubic Nonlinear Optical Properties of Dipolar Alkynylruthenium Complexes with Oligo(phenyleneethynylene) Bridges Babgi, B.; Rigamonti, L.; Cifuentes, M. P.; Corkery, T. C.; Randles, M. D.; Schwich, T.; Petrie, S.; Stranger, R.; Teshome, A.; Asselberghs, I.; Clays, K.; Samoc, M.; Humphrey, M. G. J. Am. Chem. Soc. 2009, 131, 10293-10307. <u>Abstract:</u>

$$O_2 N \longrightarrow [Ru] = trans-RuCl(dppm)_2$$

The syntheses of trans-[Ru{4,4'-C=CC<sub>6</sub>H<sub>2</sub>[2,5-(OEt)<sub>2</sub>]C=CC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>]Cl(dppm)<sub>2</sub>] (**19**), trans-[Ru{4,4',4''- $C \equiv CC_6H_4C \equiv CC_6H_2[2,5-(OEt)_2]C \equiv CC_6H_4NO_2 CI(dppm)_2]$  (20), trans-[Ru{4,4',4'',4'''-C \equiv CC\_6H\_4C \equiv CC\_6H\_2[2,5-(OEt)\_2]C \equiv CC\_6H\_4NO\_2 CI(dppm)\_2]  $(OEt)_2]C \equiv CC_6H_2[2,5-(OEt)_2]C \equiv CC_6H_4NO_2CI(dppe)_2$  (21), trans- $[Ru\{4,4',4'',4'',4''',C \equiv CC_6H_4C \equiv CC_6H_2[2,5-(OEt)_2]C \equiv CC_6H_4NO_2CI(dppe)_2$  $(OEt)_2$ ]C=CC<sub>6</sub>H<sub>2</sub>[2,5-(OEt)<sub>2</sub>]C=CC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>}Cl(dppm)<sub>2</sub>] *trans*-[Ru{4,4',4",4"'-(22),  $C \equiv CC_6H_4C \equiv CC_6H_2[2,5-(OEt)_2]C \equiv CC_6H_4NO_2 Cl(dppm)_2]$ (23), and *trans*-[Ru{4,4',4",4"',4"''- $C \equiv CC_6H_4C \equiv CC_6H_2[2,5-(OEt)_2]C \equiv CC_6H_2[2,5-(OEt)_2]C \equiv CC_6H_4NO_2]C[(dppm)_2]$ (24) are reported, together with those of precursor alkynes, complexes with the donor- $\pi$ -bridge-acceptor formulation that affords efficient quadratic and cubic NLO compounds; the identity of 19 was confirmed by a structural study. The electrochemical properties of 19–24 and related complexes with shorter  $\pi$ bridge ligands were assessed by cyclic voltammetry, and the linear optical, quadratic nonlinear optical, and cubic nonlinear optical properties were assayed by UV-vis-NIR spectroscopy, hyper-Rayleigh scattering studies at 1064 and 1300 nm, and broad spectral range femtosecond Z-scan studies, respectively. The Ru<sup>II/III</sup> oxidation potentials and wavelengths of the optical absorption maxima decrease on  $\pi$ -bridge lengthening, until the tri(phenyleneethynylene) complex is reached, further chain lengthening leaving these parameters invariant; theoretical studies employing timedependent density functional theory have shed light on this behavior. The quadratic nonlinearity  $\beta_{1064}$  and two-photon absorption cross-section reach maximal values at this same  $\pi$ -bridge length, a similar saturation behavior that may reflect a common importance of ruthenium-to-alkynyl ligand charge transfer in electronic and optical behavior in these molecules.

• Positively Charged Base Surrogate for Highly Stable "Base Pairing" through Electrostatic and Stacking Interactions

Kashida, H.; Ito, H.; Fujii, T.; Hayashi, T.; Asanuma, H. J. Am. Chem. Soc. **2009**, 131, 9928-9930. Abstract:



"Base pairs" of cationic dyes (p-methylstilbazole) were incorporated into oligodeoxyribonucleotides (ODNs). This "base pair" greatly stabilized the duplex through electrostatic and stacking interactions. The melting temperature of modified ODN was higher than those of neutral dyes and native base pairs. Further stabilization of the duplex was observed when the number of cationic dyes increased.

2

 Hybrid Cavitand Capsule with Hydrogen Bonds and Metal–Ligand Coordination Bonds: Guest Encapsulation with Anion Assistance Yamanaka, M.; Toyoda, N.; Kobayashi, K. J. Am. Chem. Soc. 2009, 131, 9880–9881.
<u>Abstract:</u>



Multifunctionalized  $C_{2v}$ -cavitand **1** was synthesized in six steps from a tetrabromo cavitand. A 1:1 mixture of **1** and **2** in CDCl<sub>3</sub> or CD<sub>2</sub>Cl<sub>2</sub> quantitatively self-assemble into a supramolecular hybrid capsule **3** through hydrogen bond and metal–ligand coordination bond. The cavity of the capsule **3** is filled with triflate ion and penetrated alkyl groups of ureides. Capsule **3** encapsulates a neutral guest molecule such as 4,4'-diiodobiphenyl (**4**) with the assistance of an anion. The encapsulation complex was identified by an NMR technique. The kinetics of guest exchange is controllable by the amounts and/or types of anions or other influences such as the polarity of the solvent.

 Using Click Chemistry To Fabricate Ultrathin Thermoresponsive Microcapsules through Direct Covalent Layer-by-Layer Assembly Huang, C.-J.; Chang, F.-C. *Macromolecules* 2009, *42*, 5155–5166.
<u>Abstract:</u>



We report the syntheses of azido- and acetylene-functionalized poly(*N*-isopropylacrylamide) (PNIPAm) copolymers and their use in the fabrication of ultrathin thermoresponsive microcapsules through direct covalent layer-by-layer (LbL) assembly using click chemistry. The clickable copolymers poly[N-isopropylacrylamide-co-(trimethylsilyl)propargylacrylamide] and poly(N-isoropylacrylamideco-3-azideopropylacrylamide) were prepared through atom transfer radical polymerization (ATRP) at 0 °C using a synthesized dansyl-labeled initiator and the CuBr/Me<sub>6</sub>TREN (hexamethylated tris[2-(dimethylamino)ethyl]amine) catalyst complex in 2-propanol. After removing the protective trimethylsilyl groups, these clickable PNIPAm copolymers assemble alternately onto azido-modified silica particles in aqueous media through click reactions catalyzed by copper sulfate and sodium ascorbate. After removing the template, the microcapsules remained stable because of the presence of the covalently bonded triazole units; the microcapsules exhibited thermoresponsive and thermoreversible swelling/deswelling behaviors upon changing the temperature of the medium. Adjusting the number of clickable functionalities resulted in changes to the degree of cross-linking, thereby allowing control over the surface morphology and thickness of the covalently stabilized PNIPAm multilayer thin films. The microcapsules fabricated close to the lower critical solution temperature of PNIPAm exhibited extremely low surface roughnesses and thick multilayer films as a result of their compact chain conformation in aqueous solution, leading to tighter packing of the

PNIPAm structure. We further postfunctionalized the surface of the multilayer thin film through click reactions with an azido-modified lissamine rhodamin dye to demonstrate the feasibility of further 3 modification with potentially useful functionalities. Finally, preliminary study on the permeability of microcapsules was presented by using different molecular weigh tetramethylrhodamine isothiocyanate (TRITC)-labeled dextran and rhodamine 6G as probe molecules, and the results revealed that the microcapsules with tighter packing wall are selectively permeable to molecules and show potential applications for the encapsulation of a variety of materials.

 Effect of Stretching on the Structure of Cylinder- and Sphere-Forming Styrene–Isoprene–Styrene Block Copolymers
Stasiak, J.; Squires, A. M.; Castelletto, V.; Hamley, I. W.; Moggridge, G. D. *Macromolecules* 2009, 42, 5256–5265.
Abstract:



Two styrene–isoprene–styrene block copolymers Vector 4111 and 4113, exhibiting cylindrical (18 wt % PS) and spherical (16 wt % PS) morphology, respectively, have been examined under uniaxial elongation up to 200% strain. On the basis of stress–strain data, mechanical properties are compared for isotropic and oriented polystyrene domains. The structure at various stages of deformation has been determined from SAXS patterns in three planes and two principal deformation directions with respect to orientation. Samples showed a very high degree of hexagonal packing, resulting in an X-ray pattern taken parallel to the cylinder alignment approaching single crystal ordering. Cylinders were aligned with the closest packed planes parallel to film surface. Particular attention has been paid to a lattice deformation process occurring during the first stretching and relaxation cycle. For a copolymer with oriented cylindrical morphology the deformation was affine up to 120% strain. The microdomain spacing was calculated parallel and perpendicular to the stretching direction. The cylindrical microstructure orientation, quantified by Hermans' orientation factor reduced during elongation of oriented polymer, while the elongation of isotropic sample caused an increase of orientation. Deformation of all studied morphologies was reversible.

 Tuning the Amphiphilicity of Building Blocks: Controlled Self-Assembly and Disassembly for Functional Supramolecular Materials Wang, Y.; Xu, H.; Zhang, X. Adv. Mater. 2009, 2849-2864. <u>Abstract:</u>



Amphiphilicity is one of the molecular bases for self-assembly. This review gives an overview on progress in controlled self-assembly and disassembly through tuning the amphiphilicity of building blocks for the fabrication of functional supramolecular materials.

• Conducting Nanocomposite Polymer Foams from Ice-Crystal-Templated Assembly of Mixtures of Colloids

Colard, C. A. L.; Cave, R. A.; Grossiord, N.; Covington, J. A.; Bon, S. A. F. Adv. Mater. 2009, 2894-2898.

Abstract:



Fabrication of conducting nanocomposite- reinforced soft polymer foams is demonstrated. These multicomponent cellular materials are built from a mixture of colloids dispersed in water by freezedrying, thereby using ice crystals as template for the porous structure. An excluded-volume effect armors the "soft"-polymer cell walls with "hard" nanoparticles, thereby enhancing the mechanical robustness of the foams.

 Selective Anion Binding in Water with Use of a Zinc(II) Dipicolylamino Functionalized Diketopiperazine Scaffold Veliscek Carolan, J.; Butler, S. J.; Jolliffe, K. A. J. Org. Chem. 2009, 74, 2992–2996. <u>Abstract:</u>



The design and synthesis of a diketopiperazine based anion receptor bearing two dipicolylamino arms complexed to zinc(II) ions is described. This receptor is readily prepared from the dipeptide precursor by a microwave-assisted intramolecular cyclization reaction. Upon addition of zinc(II), the receptor binds di- and triphosphate ions with high affinity and selectivity in aqueous solution, as determined by using a fluorescent indicator displacement assay.

 Control of the Intramolecular [2+2] Photocycloaddition in a Bis-Stilbene Macrocycle Xu, Y.; Smith, M. D.; Krause, J. A.; Shimizu, L. S. J. Org. Chem. 2009, 74, 4874–4877. <u>Abstract:</u>



The intramolecular [2+2] photocyclization of a bis-stilbene macrocycle was studied. The reaction can be controlled by the insertion and removal of urea protecting groups. Upon UV-irradiation in both the solid state and DMSO solution, the free urea macrocycle undergoes a *cis-trans* photoisomerization that is followed by a [2+2] cycloaddition to afford a single product in high yield. The presence of the triazinanone urea protecting groups does not alter the *cistrans* photoisomerization but greatly decreases the selectivity of the photocycloaddition step.

• High-spin polycationic states of an alternate meta-para-linked oligoarylamine incorporating two macrocycles.

Sakamaki, D.; Ito, A.; Furukawa, K.; Kato, T.; Tanaka, K. *Chem. Commun.* **2009**, 4524 – 4526. <u>Abstract:</u>



High-spin alignment for dicationic, tricationic, tetracationic and hexacationic species of a meta-paralinked oligoarylamine was accomplished by incorporating cyclophane skeletons into the oligomer backbone.

 Water helicate (H<sub>2</sub>O)<sub>7</sub>, hosted by a diamondoid metal–organic Framework. Hedayetullah, M.; Wang, L.; Wah, M.; Vittal, J. J. *Chem. Commun.* 2009, 4539 – 4541. <u>Abstract:</u>



A new form of water aggregate, viz.,  $(H_2O)_7$  helicate, has been trapped between the  $ClO_4^-$  anions in the channels of a diamondoid metal–organic framework (MOF) where a small change in the structure of the backbone of the MOF from 1,10-phenanthroline to a 2,2-bipyridine ligand transforms the cyclic to an acyclic water helicate.

• Stepwise Construction of Head-to-Tail-Type Oligothiophenes via Iterative Palladium-Catalyzed CH Arylation and Halogen Exchange Masuda, N.; Tanba, S.; Sugie, A.; Monguchi, D.; Koumura, N.; Hara, K.; Mori, A. *Org. Lett.* 

**2009**, *11*, 2297–2300.

Abstract:



Well-defined Head-to-Tail oligothiophene

As demand increases for oligothiophenes and polythiophenes as advanced electronic and photonic materials, such as organic TFT, liquid crystals, **photovoltaic cells**, preparative methodologies of oligothiophenes have become a significant issue in organic synthesis. In addition, recent progress of the HT-type oligothiophenes as materials for organic dye-sensitized and thin-film **photovoltaic** batteries as well as organic TFTs prompted us to develop facile synthetic strategies for such materials.

 Regioselective Ru-Catalyzed Direct 2,5,8,11-Alkylation of Perylene Bisimides Nakazono, S.; Imazaki, Y.; Yoo, H.; Yang, J.; Sasamori, T.; Tokitoh, N.; Tassel C.; Kageyama, H.; Kim, D.; Shinokubo, H.; Osuka, A. *Chem. Eur. J.* **2009**, *15*, 7530-7533.
<u>Abstract:</u>



**Regioselective** direct alkylation of perylene bisimides at 2,5,8,11-positions has been achieved by reaction with terminal alkenes under ruthenium catalysis by the Murai-Chatani-Kakiuchi protocol (see scheme). Alkylation of perylene bisimides results in enhanced solubility and quantum efficiency in

the solid state.

 Synthesis, Conformational Interconversion, and Photophysics of Tethered Porphyrin-Fullerene<sup>-</sup> Dyads with Parachute Topology
Fazio, M. A.; Durandin, A.; Tkachenko, N. V.; Niemi, M.; Lemmetyinen, H.; Schuster, D. I.

Chem. Eur. J. 2009, 15, 7698-7705.

Abstract:



The synthesis of a porphyrin-fullerene dyad with "parachute" topology is reported. To determine whether the dyad is "flexing" at room temperature, low-temperature NMR experiments were used. Computational modeling has shown the low-energy conformation of the dyad to be nonsymmetric. Although, <sup>1</sup>H NMR spectroscopy at room temperature is consistent with a molecule with  $C_{2\nu}$  symmetry, the spectrum changes on lowering the temperature consistent with "windshield wiper"-like motion, in which the porphyrin moiety rotates from one side of the C<sub>60</sub> sphere to the other. Nanosecond and picosecond fluorescence lifetime experiments show two components contribute to the fluorescence decay, also consistent with the presence of more than one conformer.

• Hierarchical Supermolecular Structures for Sustained Drug Release

Tan, J. P. K.; Kim, S. H.; Nederberg, F.; Appel, E. A.; Waymouth, R. M.; Zhang, Y.; Hedrick, J. L.; Yang, Y. Y. *Small* **2009**, *5*, 1504-1507.

Abstract:



Fiber-like supermolecular structures having hierarchical order are formed from the coassembly of stereoregular poly(ethylene glycol)-*block*-polylactide (PEG-*b*-PLA) block copolymers with paclitaxel, a well-known anticancer drug (see image). Importantly, these paclitaxel- loaded block copolymer complexes possess a PEG shell, show stable sustained release of the drug under simulated physiological conditions, and have great potential in clinical applications for localized drug delivery.

 Self-Sorted Nanotube Networks on Polymer Dielectrics for Low-Voltage Thin-Film Transistors Roberts, M. E.; LeMieux, M. C.; Sokolov, A. N.; Bao, Z. Nano Lett. 2009, 9, 2526–2531.
<u>Abstract:</u>



Recent exploitations of the superior mechanical and electronic properties of carbon nanotubes (CNTs) have led to exciting opportunities in low-cost, high performance, carbon-based electronics. In this report, low-voltage thin-film transistors with aligned, semiconducting CNT networks are fabricated on a chemically modified polymer gate dielectric using both rigid and flexible substrates. The multifunctional polymer serves as a thin, flexible gate dielectric film, affords low operating voltages, and provides a platform for chemical functionalization. The introduction of amine functionality to the dielectric surface leads to the adsorption of a network enriched with semiconducting CNTs with tunable density from spin coating a bulk solution of unsorted CNTs. The composition of the deposited CNT networks is verified with Raman spectroscopy and electrical characterization. For transistors at operating biases below 1 V, we observe an effective device mobility as high as 13.4 cm<sup>2</sup>/Vs, a subthreshold swing as low as 130 mV/dec, and typical on-off ratios of greater than 1,000. This demonstration of high performance CNT thin-film transistors operating at voltages below 1 V and deposited using solution methods on polymeric and flexible substrates is an important step toward the realization of low-cost flexible electronics.

 Peptide-Targeted Diagnostics and Radiotherapeutics Tweedle, M. F. Acc. Chem. Res. 2009, 42, 958–968.
<u>Abstract:</u>



Radiotherapeutic drugs and medical imaging agents, although used for different purposes, both benefit from precise targeting. When systemically administered, either would be most useful if designed to find and bind only a tumor, single type of cell, or unique molecular assembly thereon. In this Account, we examine the use of small peptides, natural and synthetic, to create biochemically specific molecular imaging agents and radiotherapeutic pharmaceuticals, discussing three distinct examples.

In one project, a small natural peptide known to target members of the bombesin family of receptors was chemically attached to a strong, versatile metal chelator, DO3A, through a series of small-molecule linkers. The linkers powerfully affected not only binding strength for the bombesin receptors, tissue distribution, and tumor uptake *in vivo* but also receptor subtype specificity. When the assembly is combined with an active metal ion for human trials, the versatility of the DO3A

9

(dodecanetriacetate) chelate affords choices in selecting the metal ion for different purposes: lutetium for a combination radiotherapeutic and diagnostic agent, <sup>177</sup>Lu-AMBA, and gallium for a positron emission tomography (PET) imaging agent, <sup>68</sup>Ga-AMBA.

We also created small (~5-kDa) bivalent peptides, each composed of different chemically linked peptides derived from phage display. The monomer peptides bound to the same target protein, VEGF-R2, a primary target of vascular endothelial growth factor (VEGF), the angiogenesis-stimulating protein. Several families of the monomer peptides did not compete with one another for the binding site on VEGF-R2. Their combination into fully synthetic hetero-bivalent molecules yielded subnanomolar  $K_d$  values and greater than 100-fold improvements over homo-bivalent molecules. Biological activity was evident in the hetero-bivalents, whereas none or very little existed in homo-bivalents, monomers, and monomer mixtures.

In ultrasound imaging, tiny bubbles (2  $\mu$ m in diameter) filled with inert gas can be used as effective contrast agents. By coating the shell of such bubbles with the peptide TKPPR (a tuftsin antagonist), we created contrast agents that bound unexpectedly to cultured endothelial cells expressing angiogenesis targets; the binding was attributable to a previously unnoticed and powerful multivalency effect. TKPPR binds specifically to neuropilin-1 (NP-1), a VEGF co-receptor, but only when multimerized is it avid. Tuftsin, a small peptide derived from immunoglobulin G (IgG) that binds to macrophages during inflammation, has been studied for over 30 years; the receptor has never been cloned. Our results led to new conclusions about tuftsin, NP-1, and the purpose, heretofore unknown, of exon 8 in VEGF, which appears to be involved in NP-1 binding.

Our disparate projects demonstrate that small-peptide targeted molecules can be very versatile in drug discovery in combination with classical medicinal chemistry. In particular, multivalent interactions can lead to unpredictable and useful biochemical information, as well as new drug candidates.

 Responsive MRI Agents for Sensing Metabolism *in Vivo* De Leon-Rodriguez, L. M.; Lubag, A. J. M.; Malloy, C. R.; Martinez, G. V.; Gillies, R. J.; Sherry, A. D. *Acc. Chem. Res.* 2009, *42*, 948–957. <u>Abstract:</u>



Magnetic resonance imaging (MRI) has inherent advantages in safety, three-dimensional output, and clinical relevance when compared with optical and radiotracer imaging methods. However, MRI contrast agents are inherently less sensitive than agents used in other imaging modalities primarily because MRI agents are detected indirectly by changes in either the water proton relaxation rates ( $T_1$ ,

 $T_2$ , and  $T_2^*$ ) or water proton intensities (chemical exchange saturation transfer and paramagnetic chemical exchange saturation transfer, CEST and PARACEST). Consequently, the detection limit of an MRI agent is determined by the characteristics of the background water signal; by contrast, optical and radiotracer-based methods permit direct detection of the agent itself. By virtue of responding to background water (which reflects bulk cell properties), however, MRI contrast agents have considerable advantages in "metabolic" imaging, that is, spatially resolving tissue variations in pH, redox state, oxygenation, or metabolite levels. In this Account, we begin by examining sensitivity limits in targeted contrast agents and then address contrast agents that respond to a physiological change; these responsive agents are effective metabolic imaging sensors.

The sensitivity requirements for a metabolic imaging agent are quite different from those for a targeted  $Gd^{3+}$ -based  $T_1$  agent (for example, sensing cell receptors). Targeted  $Gd^{3+}$  agents must have either an extraordinarily high water proton relaxivity ( $r_1$ ) or multiple  $Gd^{3+}$  complexes clustered together at the target site on a polymer platform or nanoparticle assembly. Metabolic MRI agents differ in that the high relaxivity requirement, although helpful, is eased because these agents respond to bulk properties of tissues rather than low concentrations of a specific biological target. For optimal sensing, metabolic imaging agents should display a large change in relaxivity ( $\Delta r_1$ ) in response to the physiological or metabolic parameter of interest.

Metabolic imaging agents have only recently begun to appear in the literature and only a few have been demonstrated *in vivo*. MRI maps of absolute tissue pH have been obtained with  $Gd^{3+}$ -based  $T_1$  sensors. The requirement of an independent measure of agent concentration in tissues complicates these experiments, but if qualitative changes in tissue pH are acceptable, then these agents can be quite useful. In this review, we describe examples of imaging extracellular pH in brain tumors, ischemic hearts, and pancreatic islets with  $Gd^{3+}$ -based pH sensors and discuss the potential of CEST and PARACEST agents as metabolic imaging sensors.

 Chiral Isotropic Liquids from Achiral Molecules Hough, L. E.; Spannuth, M.; Nakata, M.; Coleman, D. A.; Jones, C. D.; Dantlgraber, G.; Tschierske, C.; Watanabe, J.; Körblova, E.; Walba, D. M.; Maclennan, J. E.; Glaser, M. A.; Clark, N. A. Science 2009, 325, 452 – 456. Abstract:



A variety of simple bent-core molecules exhibit smectic liquid crystal phases of planar fluid layers that are spontaneously both polar and chiral in the absence of crystalline order. We found that because of

intralayer structural mismatch, such layers are also only marginally stable against spontaneous saddle splay deformation, which is incompatible with long-range order. This results macroscopically 11 isotropic fluids that possess only short-range orientational and positional order, in which the only macroscopically broken symmetry is chirality—even though the phases are formed from achiral molecules. Their conglomerate domains exhibit optical rotatory powers comparable to the highest ever found for isotropic fluids of chiral molecules.

• Helical Nanofilament Phases

Hough, L. E.; Jung, H. T.; Krüerke, D.; Heberling, M. S.; Nakata, M.; Jones, C. D.; Chen, D.; Link, D. R.; Zasadzinski, J.; Heppke, G.; Rabe, J. P.; Stocker, W.; Körblova, E.; Walba, D. M.; Glaser, M. A.; Clark, N. A. *Science* **2009**, *325*, 456-460.

Abstract:



In the formation of chiral crystals, the tendency for twist in the orientation of neighboring molecules is incompatible with ordering into a lattice: Twist is expelled from planar layers at the expense of local strain. We report the ordered state of a neat material in which a local chiral structure is expressed as twisted layers, a state made possible by spatial limitation of layering to a periodic array of nanoscale filaments. Although made of achiral molecules, the layers in these filaments are twisted and rigorously homochiral—a broken symmetry. The precise structural definition achieved in filament self-assembly enables collective organization into arrays in which an additional broken symmetry—the appearance of macroscopic coherence of the filament twist produces a liquid crystal phase of helically precessing layers.

• Soft Functional Materials Induced by Fibrillar Networks of Small Molecular Photochromic Gelators

Bhattacharya, S.; Samanta, S. K. *Langmuir* **2009**, *25*, 8378–8381. <u>Abstract:</u>



Low-molecular-mass organogelators (LMOGs) based on photochromic molecules aggregate in selected solvents to form gels through various spatio-temporal interactions. The factors that control

the mode of aggregation of the chromophoric core in the LMOGs during gelation, gelation-induced changes in fluorescence, the formation of stacked superstructures of extended  $\pi$ -conjugated systems, 12 and so forth are discussed with selected examples. Possible ways of generating various light-harvesting assemblies are proposed, and some unresolved questions, future challenges, and their possible solutions on this topic are presented.

 Anions as Efficient Chain Stoppers for Hydrogen-Bonded Supramolecular Polymers Pinault, T.; Cannizzo, C.; Andrioletti, B.; Ducouret, G.; Lequeux, F.; Bouteiller, L. *Langmuir* 2009, 25, 8404–8407.

Abstract:



The chain length of hydrogen-bonded supramolecular polymers and thus their rheological properties can be controlled by the presence of so-called chain stoppers: these monofunctional monomers are able to interact with the monomers and break the polymer chains. In this letter, we show that the use of anions, strong hydrogen bond competitors, instead of precisely designed complementary units is a very simple approach to tuning the rheology of a bisurea-based hydrogen-bonded supramolecular polymer. All of the anions tested were able to break the supramolecular chains, resulting in a dramatic drop in the viscosity of the solutions and were found to be more efficient than a previously described organic stopper. A careful study of the rheological properties of bisurea solutions in the presence of  $H_2PO_4$ , N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub> showed that the presence of this ion does not modify the nature of the bisurea supramolecular assembly. For a molar fraction of stopper of only 10<sup>-5</sup>, the viscosity of bisurea solutions decreases by a factor of 10 as a result of the formation of shorter supramolecular assemblies.

Enzyme-Responsive Controlled Release Using Mesoporous Silica Supports Capped with Lactose

Bernardos, A.; Aznar, E.; Marcos, M. D.; Martinez-Manez, R.; Sancenon, F.; Soto, J.; Barat, J. M.; Amoros, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 5884–5887. Abstract:



**The great escape**: A biocontrolled gated material has been prepared by grafting a lactose derivative onto the pore outlets of a mesoporous support. The galactosidase-induced hydrolysis of the  $\beta_1 \rightarrow 4$  glycosidic bond in the lactose moiety (red box in picture) allows the release of a dye entrapped in the pores of the hybrid material to the bulk solution.

• Multicomponent Reactions for the Synthesis of Complex Piperidine Scaffolds

Zhu, W.; Mena, M.; Jnoff, E.; Sun, N.; Pasau, P.; Ghosez, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 5880–5883.

Abstract:



**Creating diversity**: Multicomponent reactions for the synthesis of complex piperidine scaffolds lead to high levels of skeletal, functional, and stereochemical diversity in an efficient way (see scheme, X=OR, NR<sub>2</sub>). Connecting the acid chloride component to the dienophile generates polycyclic piperidine scaffolds by an intramolecular Diels-Alder reaction of the in situ generated azadienes.