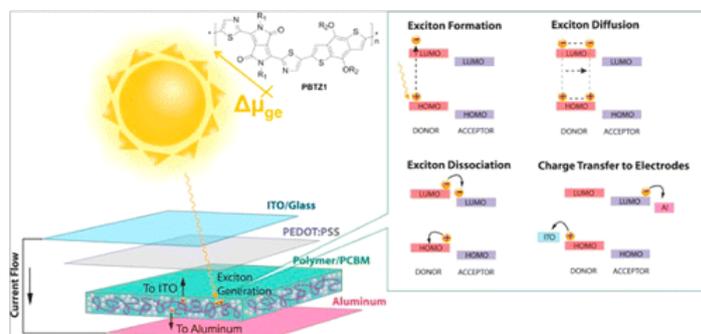


- Mediating Solar Cell Performance by Controlling the Internal Dipole Change in Organic
Carsten, B.; Szarko, J. M.; Lu, L.; Son, H. J.; He, F.; Botros, Y. Y.; Chen, L. X.; Yu, L. *Macromolecules* **2012**, *45*, 6390–6395.

1

Abstract:

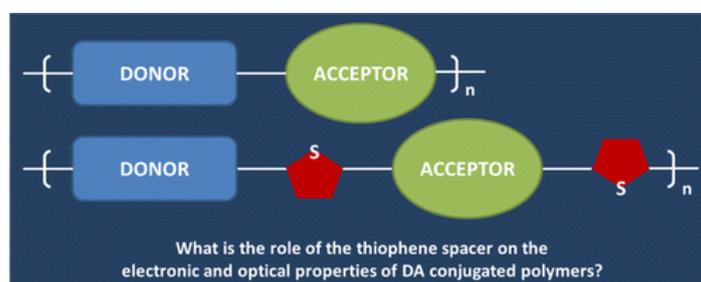


We report synthesis and characterizations of two novel series of polymers, namely the PBTZ and PBIT series. The PBTZ1 polymer was synthesized as a copolymer of 4,8-bis(2-butyloctyl)benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) along with 2,5-bis(2-ethylhexyl)-3,6-bisthiazol-2-yl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (TzDPP), while PBTZ2 was a copolymer of TzDPP and 2-(1-butylheptyl)thieno[3,4-*d*]thiazole (TTz). The PBIT series based on dithienopyrrolobenzothiadiazole (DPBT), and BDT was also synthesized. The PBIT series of polymers showed enhanced ground and excited state dipole moments (μ_g and μ_e) when compared to the previously reported PBB3 polymer, while PBTZ1 showed the largest dipole change (1.52 D) from ground to excited state ($\Delta\mu_{ge}$) in respective single polymer units. It was found that the power conversion efficiencies of the polymer series were strongly correlated to $\Delta\mu_{ge}$. The results reported demonstrate the utility of the calculated parameter $\Delta\mu_{ge}$ of single units of the polymers to predict the performance of donor–acceptor copolymers in photovoltaic devices. We rationalize this result based on the large degree of polarization in the excited state, which effectively lowers the Coulomb binding energy of the exciton in the excited state and leads to faster charge separation kinetics, thus facilitating the full separation of electron and hole.

- Donor–Acceptor Copolymers of Relevance for Organic Photovoltaics: A Theoretical Investigation of the Impact of Chemical Structure Modifications on the Electronic and Optical Properties

Pandey, L.; Risko, C.; Norton, J. E.; Brédas, J.-L. *Macromolecules* **2012**, *45*, 6405–6414.

Abstract:



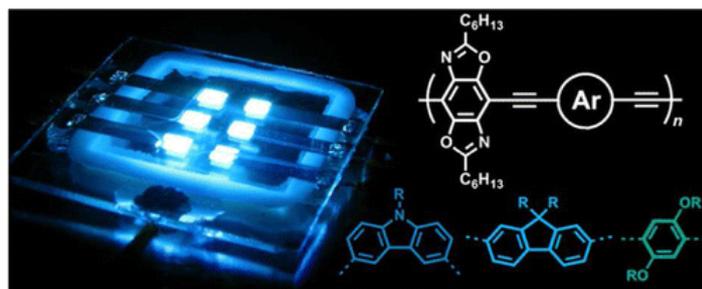
We systematically investigate at the density functional theory level how changes to the chemical structure of donor–acceptor copolymers used in a number of organic electronics applications influences the intrinsic geometric, electronic, and optical properties. We consider the combination of two distinct donors, where a central five-membered ring is fused on both sides by either a thiophene or a benzene ring, with 12 different acceptors linked to the donor either directly or through thienyl

linkages. The interplay between the electron richness/deficiency of the subunits as well as the evolution of the frontier electronic levels of the isolated donors/acceptors plays a significant role in determining the electronic and optical properties of the copolymers.

- Altering the Conjugation Pathway for Improved Performance of Benzobisoxazole-Based Polymer Guest Emitters in Polymer Light-Emitting Diodes

Intemann, J. J.; Hellerich, E. S.; Tlach, B. C.; Ewan, M. D.; Barnes, C. A.; Bhuwalka, A.; Cai, M.; Shinar, J.; Shinar, R.; Jeffries-EL, M. *Macromolecules* **2012**, *45*, 6888–6897.

Abstract:

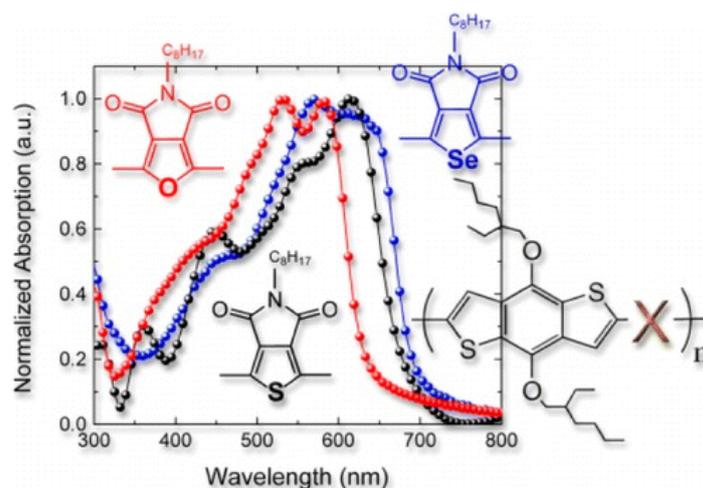


Benzobisoxazoles (BBOs) are known to increase the electron affinities and improve the electron transporting properties of materials containing them. However, BBO copolymers generally do not perform well as emissive guests in guest–host PLEDs due to inefficient Förster resonance energy transfer (FRET) between host and guest. The incomplete FRET results in a large amount of host emission and limits the potential efficiencies of the devices. In all previously reported BBO copolymers, the conjugation pathway was through the oxazole rings. Herein we report six new BBO copolymers with backbone connectivity directly on the central benzene ring, resulting in a conjugation pathway for the polymers that is perpendicular to the previously reported pathway. Guest–host PLEDs made using these polymers show that the new conjugation pathway improves FRET between the poly(*N*-vinylcarbazole) host and the BBO-containing polymer guest. Because of highly efficient FRET, no host emission is observed even at lower guest concentrations. The improved energy transfer results in devices with luminous efficiencies up to 3.1 Cd/A, a 3-fold improvement over previously reported BBO-based PLEDs. These results indicate that the conjugation pathway plays a critical role in designing emissive materials for guest–host PLEDs.

- Thieno-, Furo-, and Selenopheno[3,4-*c*]pyrrole-4,6-dione Copolymers: Effect of the Heteroatom on the Electrooptical Properties

Beaupré, S.; Pron, A.; Drouin, S. H.; Najari, A.; Mercier, L. G.; Robitaille, A.; Leclerc, M. *Macromolecules* **2012**, *45*, 6906–6914.

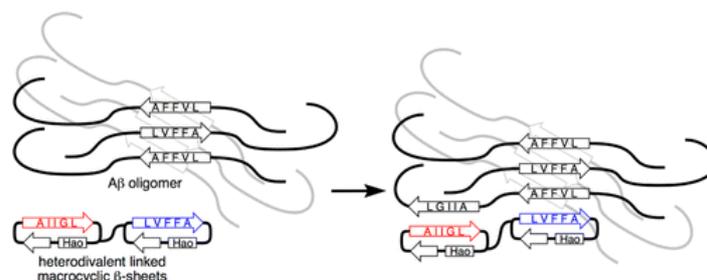
Abstract:



New push–pull conjugated polymers based on furo[3,4-*c*]pyrrole-4,6-dione (FPD) and selenopheno[3,4-*c*]pyrrole-4,6-dione (SePD) have been synthesized and compared with their thieno[3,4-*c*]pyrrole-4,6-dione (TPD) analogues to investigate the effects of the heteroatom on the electrooptical properties. The copolymers were synthesized using either Stille cross-coupling or direct heteroarylation polymerization (DHAP), the latter method giving high molecular weights. Hypsochromic shifts of the band gaps were observed for FPD-based copolymers (sulfur substituted by oxygen) while small bathochromic shift was observed for SePD (sulfur substituted by selenium) when compared to its TPD analogue. These two new classes of conjugated polymers exhibit electrooptical properties that could lead to interesting bulk heterojunction plastic solar cells.

- Heterodivalent Linked Macrocylic β -Sheets with Enhanced Activity against $A\beta$ Aggregation: Two Sites Are Better Than One
Cheng, P.-N.; Spencer, R.; Woods, R. J.; Glabe, C. G.; Nowick, J. S. *J. Am. Chem. Soc.* **2012**, *134*, 14179-14184.

Abstract:

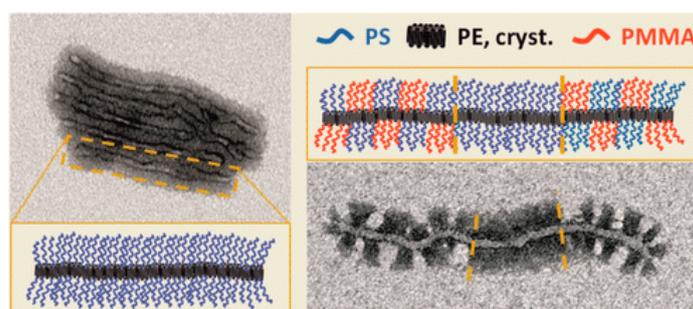


This paper reports a series of heterodivalent linked macrocyclic β -sheets **6** that are not only far more active against amyloid- β ($A\beta$) aggregation than their monovalent components **1a** and **1b** but also are dramatically more active than their homodivalent counterparts **4** and **5**. The macrocyclic β -sheet components **1a** and **1b** comprise pentapeptides derived from the N- and C-terminal regions of $A\beta$ and molecular template and turn units that enforce a β -sheet structure and block aggregation. Thioflavin T fluorescence assays show that heterodivalent linked macrocyclic β -sheets **6** delay $A\beta_{1-40}$ aggregation 6–8-fold at equimolar concentrations and substantially delay aggregation at substoichiometric concentrations, while homodivalent linked macrocyclic β -sheets **4** and **5** and monovalent macrocyclic β -sheets **1a** and **1b** only exhibit more modest effects at equimolar or greater concentrations. A model to explain these observations is proposed, in which the inhibitors bind to and stabilize the early β -structured $A\beta$ oligomers and thus delay aggregation. In this model,

heterodivalent linked macrocyclic β -sheets **6** bind to the β -structured oligomers more strongly, because N-terminal-derived component **1a** can bind to the N-terminal-based core of the β -structured oligomers, while the C-terminal-derived component **1b** can achieve additional interactions with the C-terminal region of A β . The enhanced activity of the heterodivalent compounds suggests that polyvalent inhibitors that can target multiple regions of amyloidogenic peptides and proteins are better than those that only target a single region.

- Length Control and Block-Type Architectures in Worm-like Micelles with Polyethylene Cores
Schmelz, J.; Schedl, A. E.; Steinlein, C.; Manners, I.; Schmalz, H. *J. Am. Chem. Soc.* **2012**, *134*, 14217-14225.

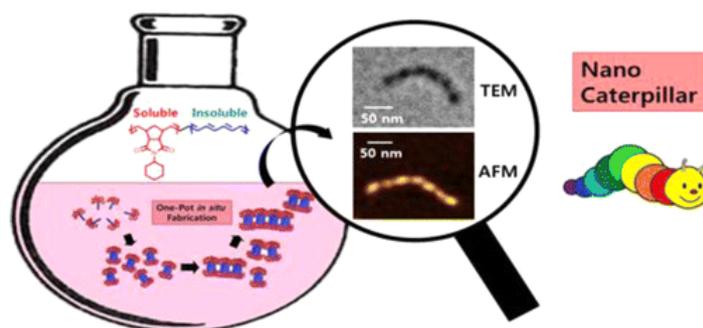
Abstract:



We present evidence for “living”-like behavior in the crystallization-driven self-assembly of triblock copolymers with crystallizable polyethylene middle blocks into worm-like crystalline-core micelles (CCMs). A new method of seed production is introduced utilizing the selective self-assembly of the triblock copolymers into spherical CCMs in appropriate solvents. Seeded growth of triblock copolymer unimers from these spherical CCMs results in worm-like CCMs with narrow length distributions and mean lengths that depend linearly on the applied unimer-to-seed ratio. Depending on the applied triblock copolymer, polystyrene-*block*-polyethylene-*block*-polystyrene (SES) or polystyrene-*block*-polyethylene-*block*-poly(methyl methacrylate) (SEM), well-defined worm-like CCMs with a homogeneous or patch-like corona, respectively, can be produced. In a subsequent step, these worm-like CCMs can be used as seeds for the epitaxial growth of a different polyethylene containing triblock copolymer. In this manner, ABA-type triblock *co*-micelles containing blocks with a homogeneous polystyrene corona and those with a patch-like polystyrene/poly(methyl methacrylate) corona were prepared. While the epitaxial growth of SEM unimers from worm-like SES CCMs with a homogeneous corona yields triblock *co*-micelles almost quantitatively, the addition of SES unimers to patchy SEM wCCMs results in a mixture of ABA- and AB-type block *co*-micelles together with residual patchy wCCMs. Following reports on self-assembled block-type architectures from polymers containing core-forming polyferrocenylsilane blocks, these structures represent the first extension of the concept to block *co*-micelles from purely organic block copolymers.

- One-Pot in Situ Fabrication of Stable Nanocaterpillars Directly from Polyacetylene Diblock Copolymers Synthesized by Mild Ring-Opening Metathesis Polymerization
Yoon, K.-Y.; Lee, I.-H.; Kim, K. O.; Jang, J.; Lee, E.; Choi, T.-L. *J. Am. Chem. Soc.* **2012**, *134*, 14291-14294.

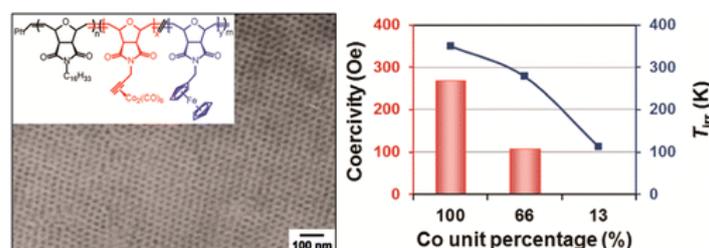
Abstract:



We report a direct one-pot route for the preparation of supramolecules from simple polyacetylene diblock copolymers synthesized by mild ring-opening metathesis polymerization of cyclooctatetraene. This in situ nanoparticlization of conjugated polymer (INCP) approach is advantageous over conventional self-assembly processes because this method does not require any tedious postsynthetic treatments. Also, this direct approach provides intriguing supramolecules with a unique nanostructure resembling a caterpillar. Furthermore, the new supramolecules are highly stable adducts because the polyacetylene core block provides an exceptionally strong driving force for the self-assembly. Even though pristine polyacetylene is unstable in air, the polyacetylene segment in the nanocaterpillar is very stable because it is protected within the shell of the supramolecule.

- Nanostructured Block-Random Copolymers with Tunable Magnetic Properties
Zha, Y.; Thaker, H. D.; Maddikeri, R. R.; Gido, S. P.; Tuominen, M. T.; Tew, G. N. *J. Am. Chem. Soc.* **2012**, *134*, 14534-14541.

Abstract:

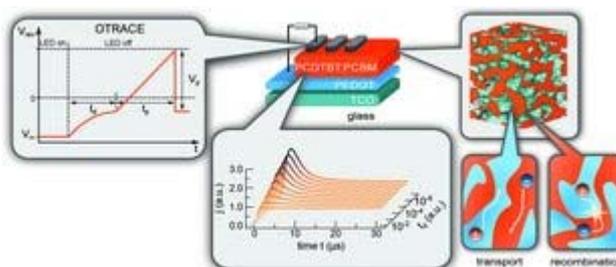


It was recently shown that block copolymers (BCPs) produced room-temperature ferromagnetic materials (RTFMs) due to their nanoscopic ordering and the cylindrical phase yielded the highest coercivity. Here, a series of metal-containing block-random copolymers composed of an alkyl-functionalized homo block (C_{16}) and a random block of cobalt complex- (Co) and ferrocene-functionalized (Fe) units was synthesized via ring-opening metathesis polymerization. Taking advantage of the block-random architecture, the influence of dipolar interactions on the magnetic properties of these nanostructured BCP materials was studied by varying the molar ratio of the Co units to the Fe units, while maintaining the cylindrical phase-separated morphology. DC magnetic measurements, including magnetization versus field, zero-field-cooled, and field-cooled, as well as AC susceptibility measurements showed that the magnetic properties of the nanostructured BCP materials could be easily tuned by diluting the cobalt density with Fe units in the cylindrical domains. Decreasing the cobalt density weakened the dipolar interactions of the cobalt nanoparticles, leading to the transition from a room temperature ferromagnetic (RTF) to a superparamagnetic material. These results confirmed that dipolar interactions of the cobalt nanoparticles within the phase-separated domains were responsible for the RTF properties of the nanostructured BCP materials.

- A New Approach for Probing the Mobility and Lifetime of Photogenerated Charge Carriers in Organic Solar Cells Under Real Operating Conditions

Baumann, A.; Lorrmann, J.; Rauh, D.; Deibel, C.; Dyakonov, V. *Adv. Mater.* **2012**, *24*, 4381–4386.

Abstract:

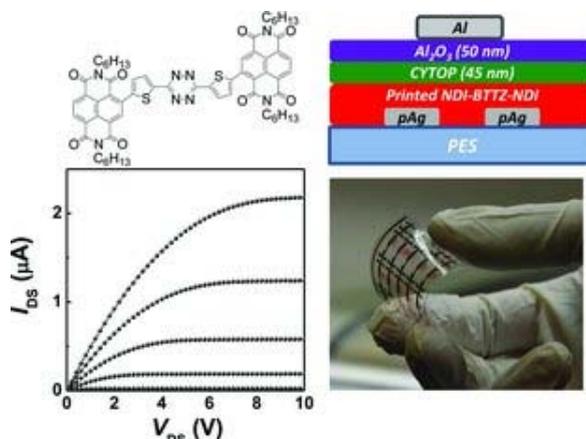


A new transient charge extraction technique is presented, which facilitates simultaneous measurements of mobility and lifetime of photogenerated charge carriers in organic solar cells under real operating conditions. An adaptive field control is implemented keeping the solar cell at open circuit conditions during recombination. The practical benefit of the new technique is demonstrated by determining the mobility-lifetime parameter of solar cells based on PCDTBT:PC₇₁BM and P3HT:PC₆₁BM.

- Stable Solution-Processed Molecular *n*-Channel Organic Field-Effect Transistors

Hwang, D. K.; Dasari, R. R.; Fenoll, M.; Alain-Rizzo, V.; Dindar, A.; Shim, J. W.; Deb, N.; Fuentes-Hernandez, C.; Barlow, S.; Bucknall, D. G.; Audebert, P.; Marder, S. R.; Kippelen, B. *Adv. Mater.* **2012**, *24*, 4445–4450.

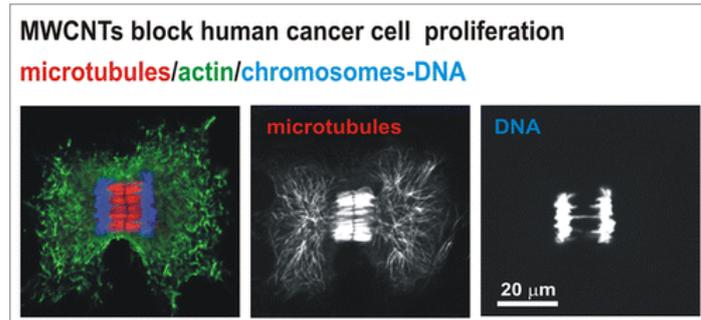
Abstract:



A new solution-processable small-molecule containing electron-poor naphthalene diimide and tetrazine moieties has been synthesized. The optimized spin-coated *n*-channel OFETs on glass substrate shows electron mobility value up to $0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Inkjet-printed OFETs are fabricated in ambient atmosphere on flexible plastic substrates, which exhibits an electron mobility value up to $0.17 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and also shows excellent environmental and operational stability.

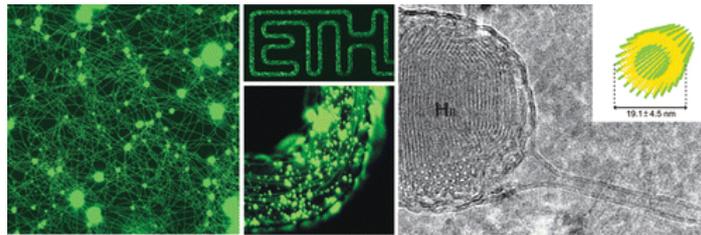
- Multiwalled Carbon Nanotubes Display Microtubule Biomimetic Properties in Vivo, Enhancing Microtubule Assembly and Stabilization

Rodriguez-Fernandez, L.; Valiente, R.; Gonzalez, J.; Villegas, J. C.; Fanarraga, M. L. *ACS Nano* **2012**, *6*, 6614–6625.

Abstract:

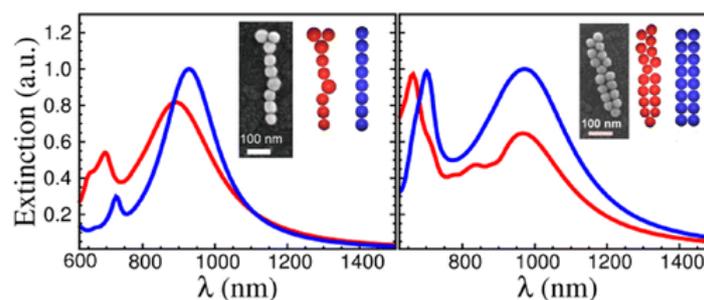
Microtubules are hollow protein cylinders of 25 nm diameter which are implicated in cytokinesis and proliferation in all eukaryotic cells. Here we demonstrate *in vivo* how multiwalled carbon nanotubes (MWCNTs) interact with microtubules in human cancer cells (HeLa) blocking mitosis and leading to cell death by apoptosis. Our data suggest that, inside the cells, MWCNTs display microtubule biomimetic properties, assisting and enhancing noncentrosomal microtubule polymerization and stabilization. These features might be useful for developing a revolutionary generation of chemotherapeutic agents based on nanomaterials.

- Directed Self-Assembly of Lipid Nanotubes from Inverted Hexagonal Structures
Sugihara, K.; Chami, M.; Derényi, I.; Vörös, J.; Zambelli, T. *ACS Nano* **2012**, *6*, 6626-6632.

Abstract:

Conventional lipid-tube formation is based on either a tube phase of certain lipids or the shape transformation of lamellar structures by applying a point load. In the present study, lipid blocks in inverted hexagonal phase made of 1,2-dioleoyl-*sn*-glycero-3-phosphoethanolamine (DOPE) were shown to protrude lipid nanotubes upon a fluid-dynamic flow on polyelectrolyte-functionalized surfaces in physiological buffer solution. The outer diameter of the tubes is 19.1 ± 4.5 nm and their lengths are up to several hundred micrometers. The method described enables the alignment and patterning of lipid nanotubes into various (including curvy) shapes with a microfluidic system.

- Toward Plasmonic Polymers
Slaughter, L. S.; Willingham, B. A.; Chang, W.-S.; Chester, M. H.; Ogden, N.; Link, S. *Nano Letters* **2012**, *12*, 3967-3972.

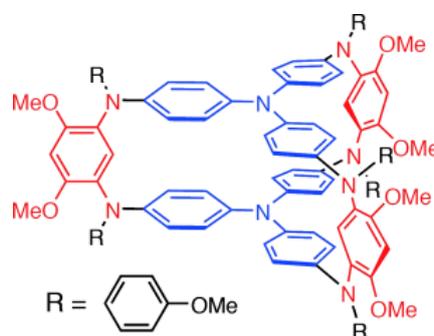
Abstract:

We establish the concept of a plasmonic polymer, whose collective optical properties depend on the repeat unit. Experimental and theoretical analyses of the super- and sub-radiant plasmon response of plasmonic polymers comprising repeat units of single nanoparticles or dimers of gold nanoparticles show that (1) the redshift of the lowest energy coupled mode becomes minimal as the chain approaches the infinite chain limit at a length of ~ 10 particles, (2) the presence and energy of the modes are sensitive to the geometries of the constituents, that is, repeat unit, but (3) spatial disorder and nanoparticle heterogeneity have only small effects on the super-radiant mode.

- A Triphenylamine Double-Decker: From a Delocalized Radical Cation to a Diradical Dication with an Excited Triplet State

Yokoyama, Y.; Sakamaki, D.; Ito, A.; Tanaka, K.; Shiro, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 9403-9406.

Abstract:



The redox properties and electronic structures of polycationic species were examined using a triphenylamine double-decker species. The double-decker has a strong electron-donating ability, and the spin in the radical cation is delocalized over the whole caged skeleton, despite no direct transannular π - π interaction between two TPA decks. Moreover, the diradical dication has spin-singlet character, despite the meta-phenylene linkage.

- Preparation of Organotrifluoroborate Salts: Precipitation-Driven Equilibrium under Non-Etching Conditions

Lennox, A. J. J.; Lloyd-Jones, G. C. *Angew. Chem. Int. Ed.* **2012**, *51*, 9385-9388.

Abstract:



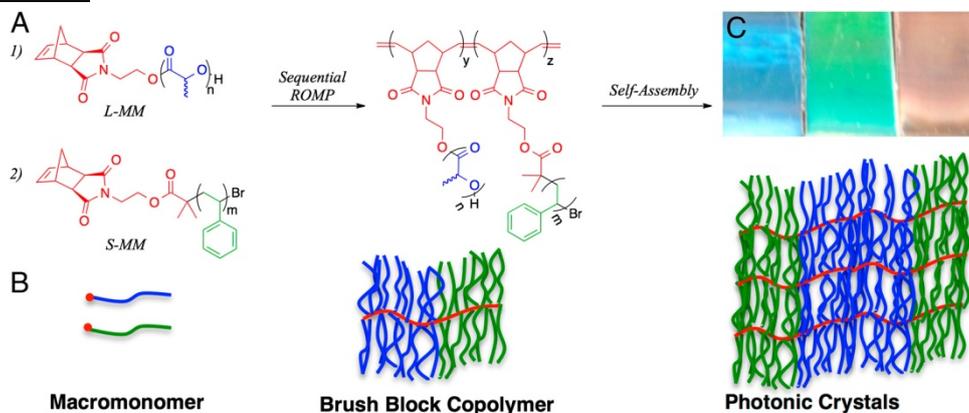
Simple, rapid, and scaleable: In contrast to current procedures using corrosive HF/MF or MHF₂ reagents (M=e.g. K), a wide range of trifluoroborates can be rapidly, simply, and safely prepared from MF (M=K, Cs), RCO₂H, and a boronic acid/ester in regular glassware (see figure; left versus right). The use of L-(+)-tartaric acid as an alkali-metal sponge is key and allows isolation of RBF₃M by a simple stir/filter/evaporate sequence.

- Rapid self-assembly of brush block copolymers to photonic crystals.

Sveinbjörnsson, B. R.; Weitekamp, R. A.; Miyake, G. M.; Xia, Y.; Atwater, H. A.; Grubbs, R. H. *Proc. Nat. Acad. Sci. USA* **2012**, *109*, 14332-14336.

9

Abstract:

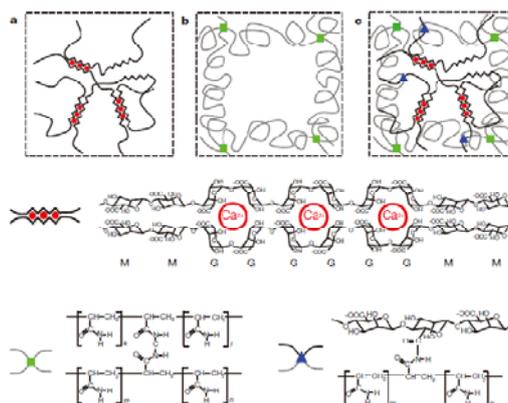


The reduced chain entanglement of brush polymers over their linear analogs drastically lowers the energetic barriers to reorganization. In this report, we demonstrate the rapid self-assembly of brush block copolymers to nanostructures with photonic bandgaps spanning the entire visible spectrum, from ultraviolet (UV) to near infrared (NIR). Linear relationships were observed between the peak wavelengths of reflection and polymer molecular weights. This work enables “bottom-up” fabrication of photonic crystals with application-tailored bandgaps, through synthetic control of the polymer molecular weight and the method of self-assembly. These polymers could be developed into NIR-reflective paints, to combat the “urban heat island effect” due to NIR photon thermalization.

- Highly stretchable and tough hydrogels.

Sun, J.-Y.; Zhao, X.; Illeperuma, W. R. K.; Chaudhuri, O.; Oh, K. H.; Mooney, D. J.; Vlassak, J. J.; Suo, Z. *Nature* **2012**, *489*, 133-136.

Abstract:



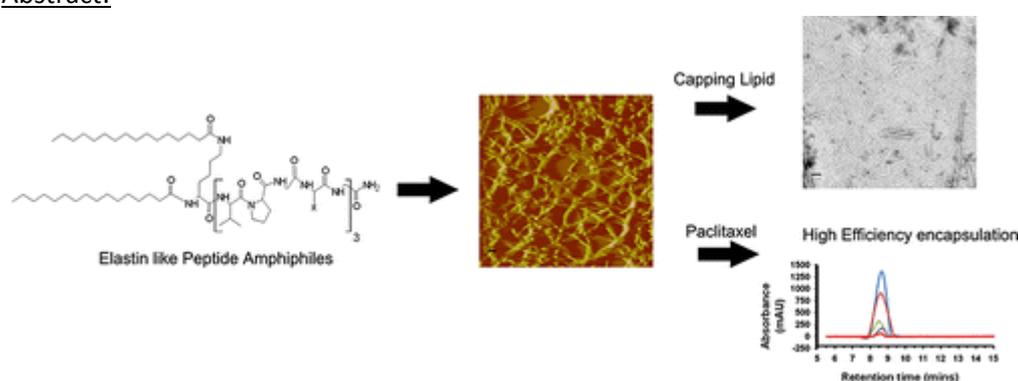
Hydrogels are used as scaffolds for tissue engineering, vehicles for drug delivery, actuators for optics and fluidics, and model extracellular matrices for biological studies. The scope of hydrogel applications, however, is often severely limited by their mechanical behaviour. Most hydrogels do not exhibit high stretchability; for example, an alginate hydrogel ruptures when stretched to about 1.2 times its original length. Some synthetic elastic hydrogels have achieved stretches in the range 10-20, but these values are markedly reduced in samples containing notches. Most hydrogels are brittle, with fracture energies of about 10 Jm^{-2} , as compared with $1,000 \text{ Jm}^{-2}$ for cartilage⁹ and $10,000 \text{ Jm}^{-2}$ for natural rubbers. Intense efforts are devoted to synthesizing hydrogels with improved

mechanical properties; certain synthetic gels have reached fracture energies of $100\text{--}1,000\text{ Jm}^{-2}$. Here we report the synthesis of hydrogels from polymers forming ionically and covalently crosslinked networks. Although such gels contain 90 % water, they can be stretched beyond 20 times their initial length, and have fracture energies of $9,000\text{ Jm}^{-2}$. Even for samples containing notches, a stretch of 17 is demonstrated. We attribute the gels' toughness to the synergy of two mechanisms: crack bridging by the network of covalent crosslinks, and hysteresis by unzipping the network of ionic crosslinks. Furthermore, the network of covalent crosslinks preserves the memory of the initial state, so that much of the large deformation is removed on unloading. The unzipped ionic crosslinks cause internal damage, which heals by re-zipping. These gels may serve as model systems to explore mechanisms of deformation and energy dissipation, and expand the scope of hydrogel applications.

- Elastin-Like Peptide Amphiphiles Form Nanofibers with Tunable Length

Aluri, S.; Pastuszka, M. K.; Moses, A. S.; MacKay, J. A. *Biomacromolecules* **2012**, *13*, 2645-2654.

Abstract:



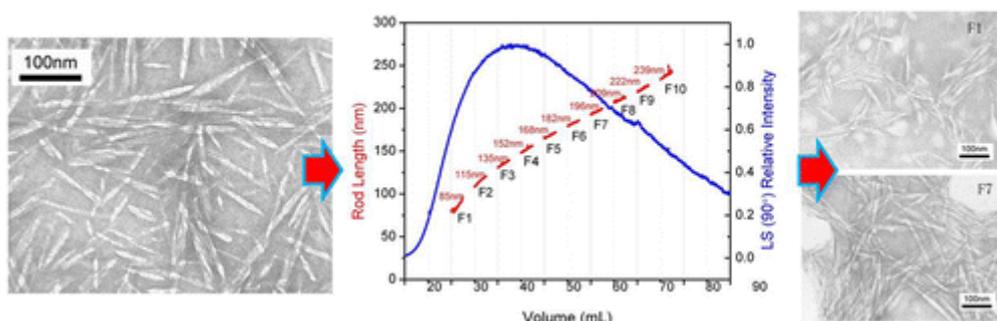
Peptide amphiphiles (PAs) self-assemble nanostructures with potential applications in drug delivery and tissue engineering. Some PAs share environmentally responsive behavior with their peptide components. Here we report a new type of PAs biologically inspired from human tropoelastin. Above a lower critical solution temperature (LCST), elastin-like polypeptides (ELPs) undergo a reversible inverse phase transition. Similar to other PAs, elastin-like PAs (ELPAs) assemble micelles with fiber-like nanostructures. Similar to ELPs, ELPAs have inverse phase transition behavior. Here we demonstrate control over the ELPAs fiber length and cellular uptake. In addition, we observed that both peptide assembly and nanofiber phase separation are accompanied by a distinctive secondary structure attributed primarily to a type-1 β turn. We also demonstrate increased solubility of hydrophobic paclitaxel (PAX) in the presence of ELPAs. Due to their biodegradability, biocompatibility, and environmental responsiveness, elastin-inspired biopolymers are an emerging platform for drug and cell delivery; furthermore, the discovery of ELPAs may provide a new and useful approach to engineer these materials into stimuli-responsive gels and drug carriers.

- Asymmetric Flow Field-Flow Fractionation with Multiangle Light Scattering Detection for Characterization of Cellulose Nanocrystals

Guan, X.; Cueto, R.; Russo, P.; Qi, Y.; Wu, Q. *Biomacromolecules* **2012**, *13*, 2671-2679.

Abstract:

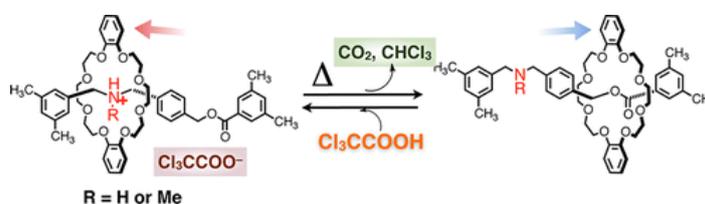
Asymmetric Flow Field-Flow Fractionation of Cellulose Nano Crystals



Cellulose nanocrystals (CNCs) were analyzed by asymmetric flow field-flow fractionation (AF4) coupled with multiangle light scattering (MALS) detection. Small fractions were collected from the output of the AF4 apparatus for investigation by transmission electron microscopy (TEM). The influence of CNC injection amount, the number of passes through a high-pressure homogenizer, and different CNC sources on the elution behavior and particle size distribution was investigated. The AF4-MALS results on crystal length were compared with those from TEM. Peak distortion and variation in elution profiles with the increase in sample load were observed. Good resolution was obtained when the injection mass varied from 20 to 40 μg , corresponding to injections of 4–8 μL at a starting concentration of $\sim 5 \mu\text{g}/\mu\text{L}$; concentrations during the separation process and at the detector were significantly lower. As the number of homogenization treatments increased, the peak shape became narrower and more symmetrical. This indicates a narrowed crystal length distribution, but regardless of source or homogenization treatment, no CNC preparation was as uniform as tobacco mosaic virus, a well-known rigid rod model structure, whose length was found by AF4-MALS to be in agreement with literature values. CNCs derived from cotton contained longer crystals than those derived from microcrystalline cellulose, as shown by both AF4-MALS and TEM techniques. An advantage of AF4-MALS compared to TEM is the ability to sample large numbers of rodlike particles, which is challenging and time-consuming for TEM image analysis, especially without the presorting afforded by AF4. The good TMV results suggest a high degree of accuracy will pertain to the CNC size distribution measurements.

- Thermoresponsive Shuttling of Rotaxane Containing Trichloroacetate Ion
Abe, Y.; Okamura, H.; Nakazono, K.; Koyama, Y.; Uchida, S.; Takata, T. *Org. Lett.* **2012**, *14*, 4122-4125.

Abstract:

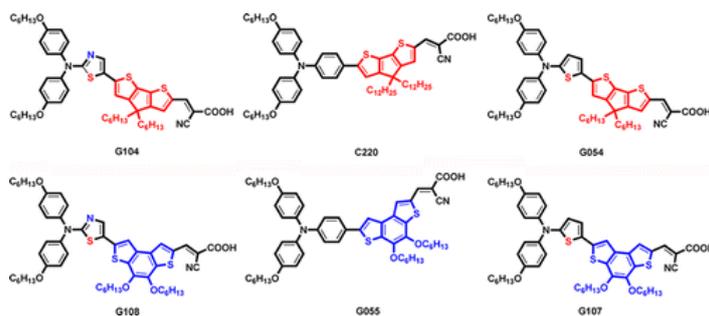


A thermoresponsive rotaxane shuttling system was developed with a trichloroacetate counteranion of an ammonium/crown ether-type rotaxane. Chemoselective thermal decomposition of the ammonium trichloroacetate moiety on the rotaxane yielded the corresponding nonionic rotaxane accompanied by a positional change of the crown ether on the axle. The rotaxane skeleton facilitated effective dissociation of the acid, markedly lowering the thermal decomposition temperature.

- Fine-tuning the Electronic Structure of Organic Dyes for Dye-Sensitized Solar Cells

Gao, P.; Tsao, H. N.; Grätzel, M.; Nazeeruddin, M. K. *Org. Lett.* **2012**, *14*, 4330-4333.

Abstract:

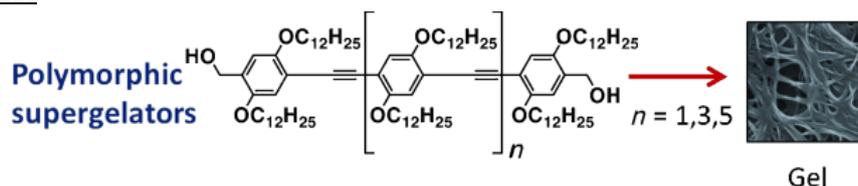


A series of metal-free organic dyes exploiting different combinations of (hetero)cyclic linkers (benzene, thiophene, and thiazole) and bridges (4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) and benzodithiophene (BDT)) as the central π -spacers were synthesized and characterized. Among them, the sensitizer containing the thiophene and CPDT showed the most broad incident photon-to-current conversion efficiency spectra, resulting in a solar energy conversion efficiency (η) of 6.6%.

- Oligo(*p*-phenylene-ethynylene)-Derived Super- π -Gelators with Tunable Emission and Self-Assembled Polymorphic Structures

Gopal, A.; Varghese, R.; Ajayaghosh, A. *Chem. Asian J.* **2012**, *7*, 2061–2067.

Abstract:

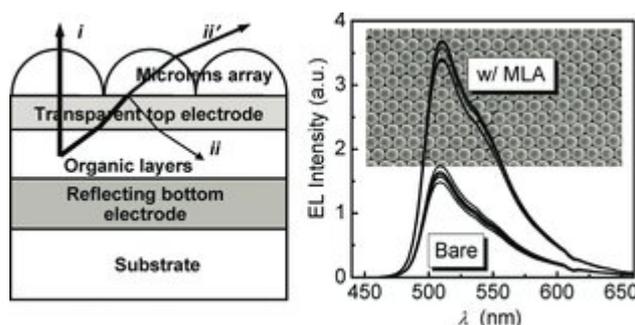


Linear π -conjugated oligomers are known to form organogels through noncovalent interactions. Herein, we report the effect of π -repeat units on the gelation and morphological properties of three different oligo(*p*-phenylene-ethynylene)s: **OPE3**, **OPE5**, and **OPE7**. All of these molecules form fluorescent gels in nonpolar solvents at low critical gel concentrations, thereby resulting in a blue gel for **OPE3**, a green gel for **OPE5**, and a greenish yellow gel for **OPE7**. The molecule–molecule and molecule–substrate interactions in these OPEs are strongly influenced by the conjugation length of the molecules. Silicon wafer suppresses substrate–molecule interactions whereas a mica surface facilitates such interactions. At lower concentrations, **OPE3** formed vesicular assemblies and **OPE5** gave entangled fibers, whereas **OPE7** resulted in spiral assemblies on a mica surface. At higher concentrations, **OPE3** and **OPE5** resulted in super-bundles of fibers and flowerlike short-fiber agglomerates when different conditions were applied. The number of polymorphic structures increases on increasing the conjugation length, as seen in the case of **OPE7** with $n=5$, which resulted in a variety of exotic structures, the formation of which could be controlled by varying the substrate, concentration, and humidity.

- Enhancing Light Extraction in Top-Emitting Organic Light-Emitting Devices Using Molded Transparent Polymer Microlens Arrays

Wrzesniewski, E.; Eom, S.-H.; Cao, W.; Hammond, W. T.; Lee, S.; Douglas, E. P.; Xue, J. *Small* **2012**, *8*, 2647–2651.

Abstract:

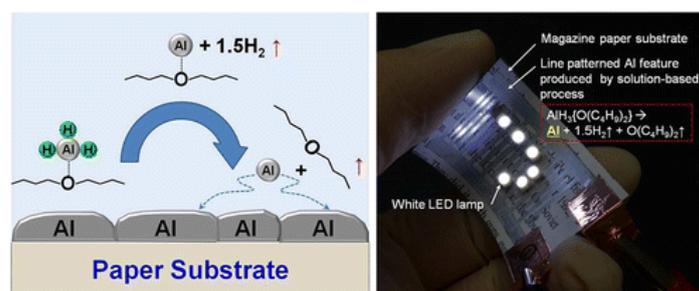


The light extraction efficiency in organic light-emitting devices (OLEDs) is enhanced by up to 2.6 times when a close-packed, hemispherical transparent polymer microlens array (MLA) is molded on the light-emitting surface of a top-emitting device. The microlens array helps to extract the waveguided optical emission in the organic layers and the transparent top electrode, and can be manufactured in large area with low cost.

- Solution Processed Aluminum Paper for Flexible Electronics

Lee, H. M.; Lee, H. B.; Jung, D. S.; Yun, J.-Y.; Ko, S. H.; Park, S. B. *Langmuir* **2012**, *28*, 13127-13135.

Abstract:

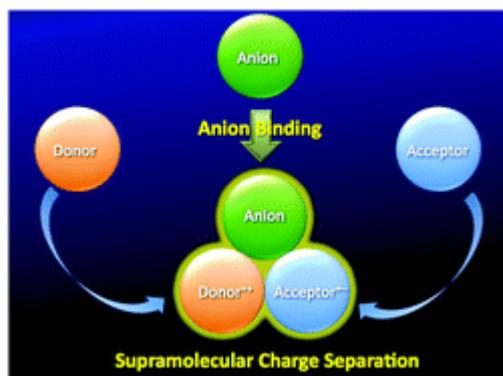


As an alternative to vacuum deposition, preparation of highly conductive papers with aluminum (Al) features is successfully achieved by the solution process consisting of Al precursor ink ($\text{AlH}_3[\text{O}(\text{C}_4\text{H}_9)_2]_2$) and low temperature stamping process performed at 110 °C without any serious hydroxylation and oxidation problems. Al features formed on several kinds of paper substrates (calendar, magazine, and inkjet printing paper substrates) are less than ~60 nm thick, and their electrical conductivities were found to be as good as thermally evaporated Al film or even better ($\leq 2 \Omega/\square$). Strong adhesion of Al features to paper substrates and their excellent flexibility are also experimentally confirmed by TEM observation and mechanical tests, such as tape and bending tests. The solution processed Al features on paper substrates show different electrical and mechanical performance depending on the paper type, and inkjet printing paper is found to be the best substrate with high and stable electrical and mechanical properties. The Al conductive papers produced by the solution process may be applicable in disposal paper electronics.

- Supramolecular electron transfer by anion binding

Fukuzumi, F.; Ohkubo, K.; D'Souza, F.; L. Sessler, J. *Chem. Commun.* **2012**, *48*, 9801-9815.

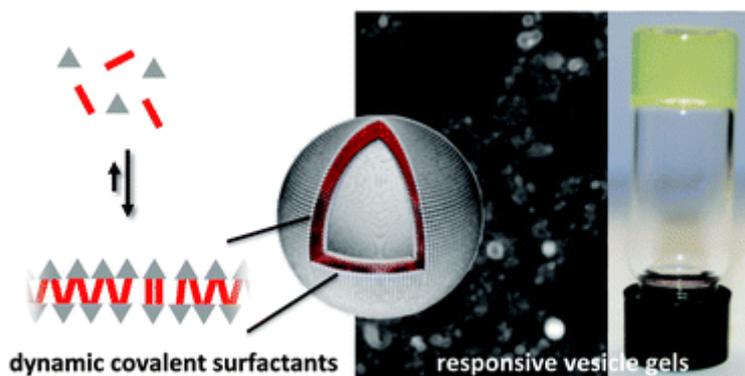
Abstract:



Anion binding provides a unique way of switching supramolecular electron-transfer reactions in certain instances through competition with cation binding.

- Dynamic covalent assembly of stimuli responsive vesicle gels
Minkenberg, C. B.; Hendriksen, W. E.; Li, F.; Mendes, E.; Eelkema, R.; H. van Esch, J. *Chem. Commun.* **2012**, 48, 9837-9839.

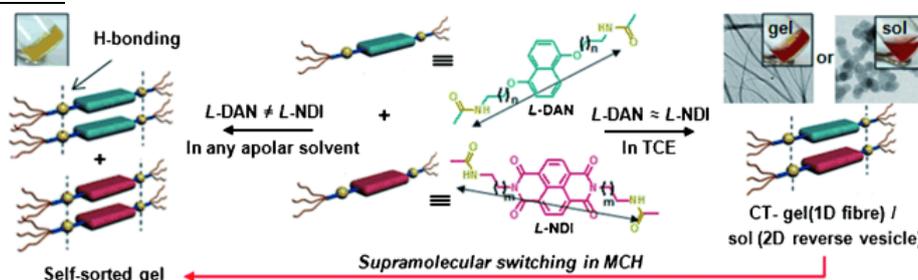
Abstract:



Stimuli-responsive vesicle gels from polymerised dynamic covalent surfactants were reversibly formed by mixing of soluble surfactant precursors in water.

- Hydrogen-Bonding Induced Alternate Stacking of Donor (D) and Acceptor (A) Chromophores and their Supramolecular Switching to Segregated States
Das, A.; Molla, M. R.; Maity, B.; Koley, D.; Ghosh, S. *Chem. Eur. J.* **2012**, 18, 9849–9859.

Abstract:

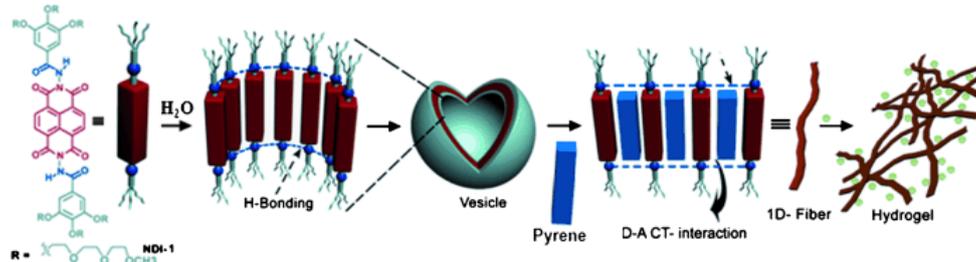


This paper reports comprehensive studies on the mixed assembly of bis-(trialkoxymethyl)-functionalized dialkoxynaphthalene (DAN) donors and naphthalene-diimide (NDI) acceptors due to the cooperative effects of hydrogen bonding, charge-transfer (CT) interactions, and solvophobic effects. A series of DAN as well as NDI building blocks have been examined (wherein the relative distance between the two amide groups in a particular chromophore is the variable structural parameter) to

understand the structure-dependent variation in mode of supramolecular assembly and morphology (organogel, reverse vesicle, etc.) of the self-assembled material. Interestingly, it was observed that when the amide functionalities are introduced to enhance the self-assembly propensity, the mode of co-assembly among the DAN and NDI chromophores no longer remained trivial and was dictated by a relatively stronger hydrogen-bonding interaction instead of a weak CT interaction. Consequently, in a highly non-polar solvent like methylcyclohexane (MCH), although kinetically controlled CT-gelation was initially noticed, within a few hours the system sacrificed the CT-interaction and switched over to the more stable self-sorted gel to maximize the gain in enthalpy from the hydrogen-bonding interaction. In contrast, in a relatively less non-polar solvent such as tetrachloroethylene (TCE), in which the strength of hydrogen bonding is inherently weak, the contribution of the CT interaction also had to be accounted for along with hydrogen bonding leading to a stable CT-state in the gel or solution phase. The stability and morphology of the CT complex and rate of supramolecular switching (from CT to segregated state) were found to be greatly influenced by subtle structural variation of the building blocks, solvent polarity, and the DAN/NDI ratio. For example, in a given D–A pair, by introducing just one methylene unit in the spacer segment of either of the building blocks a complete change in the mode of co-assembly (CT state or segregated state) and the morphology (1D fiber to 2D reverse vesicle) was observed. The role of solvent polarity, structural variation, and D/A ratio on the nature of co-assembly, morphology, and the unprecedented supramolecular-switching phenomenon have been studied by detail spectroscopic and microscopic experiments in a gel as well as in the solution state and are well supported by DFT calculations.

- Hydrogen-Bonding-Mediated Vesicular Assembly of Functionalized Naphthalene–Diimide-Based Bolaamphiphile and Guest-Induced Gelation in Water
Molla, M. R.; Ghosh, S. *Chem. Eur. J.* **2012**, *18*, 9860–9869.

Abstract:



This paper describes the spontaneous vesicular assembly of a naphthalene–diimide (NDI)-based non-ionic bolaamphiphile in aqueous medium by using the synergistic effects of π -stacking and hydrogen bonding. Site isolation of the hydrogen-bonding functionality (hydrazide), a strategy that has been adopted so elegantly in nature, has been executed in this system to protect these moieties from the bulk water so that the distinct role of hydrogen bonding in the self-assembly of hydrazide-functionalized NDI building blocks could be realized, even in aqueous solution. Furthermore, the electron-deficient NDI-based bolaamphiphile could engage in donor–acceptor (D–A) charge-transfer (CT) interactions with a water-insoluble electron-rich pyrene donor by virtue of intercalation of the latter chromophore in between two NDI building blocks. Remarkably, even when pyrene was located between two NDI blocks, intermolecular hydrogen-bonding networks between the NDI-linked hydrazide groups could be retained. However, time-dependent AFM studies revealed that the radius of curvature of the alternately stacked D–A assembly increased significantly, thereby leading to intervesicular fusion, which eventually resulted in rupturing of the membrane to form 1D fibers. Such

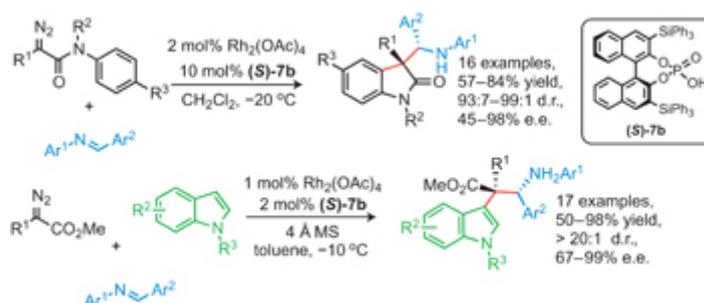
2D-to-1D morphological transition produced CT-mediated hydrogels at relatively higher concentrations. Instead of pyrene, when a water-soluble carboxylate-functionalized pyrene derivative was used as the intercalator, non-covalent tunable in-situ surface-functionalization could be achieved, as evidenced by the zeta-potential measurements.

16

- Highly enantioselective trapping of zwitterionic intermediates by imines

Qiu, H.; Li, M.; Jiang, L-Q.; Lv, F-P.; Zan, L.; Zhai, C-W.; Doyle, M. P.; Hu, W-H. *Nature Chemistry* **2012**, *4*, 733–738.

Abstract:

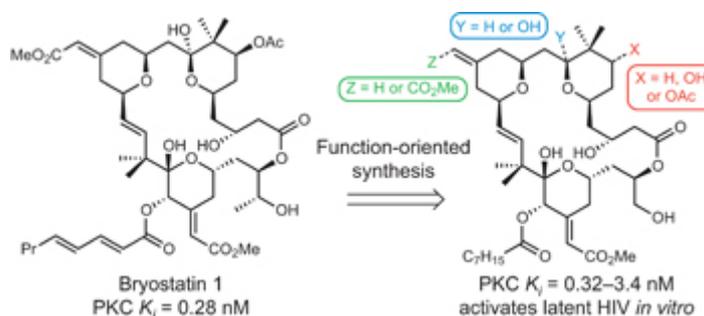


Reactions with the unstable and highly reactive zwitterionic intermediates generated in processes catalysed by transition metals are providing new opportunities for molecular constructions. Insertion reactions involve the collapse of zwitterionic intermediates, but trapping them would allow structural elaborations that are not currently available. To synthesize complex molecules in this manner, reactive electrophiles can be used to trap the zwitterionic intermediates. Here, we describe the use of imines, activated by chiral organocatalysts, and a highly efficient integrated rhodium and chiral Brønsted acid co-catalysed process to trap zwitterionic intermediates that have been proposed previously to undergo a formal C–H insertion reaction, allowing us to obtain polyfunctionalized indole and oxindole derivatives in a single step with excellent diastereoselectivity and enantioselectivity.

- Designed, synthetically accessible bryostatin analogues potently induce activation of latent HIV reservoirs in vitro

DeChristopher, B. A.; Loy, B. A.; Marsden, M. D.; Schrier, A. J.; Zack, J. A.; Wender, P. A. *Nature Chemistry* **2012**, *4*, 705–710.

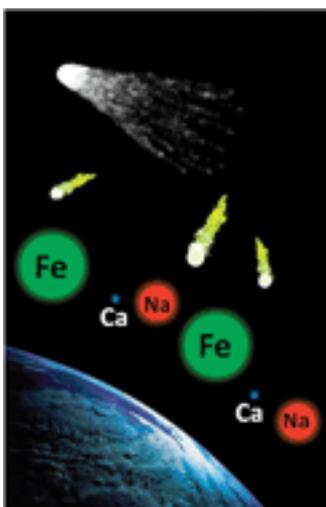
Abstract:



Bryostatin is a unique lead in the development of potentially transformative therapies for cancer, Alzheimer's disease and the eradication of HIV/AIDS. However, the clinical use of bryostatin has been hampered by its limited supply, difficulties in accessing clinically relevant derivatives, and side effects. Here, we address these problems through the step-economical syntheses of seven members of a new family of designed bryostatin analogues using a highly convergent Prins-macrocyclization

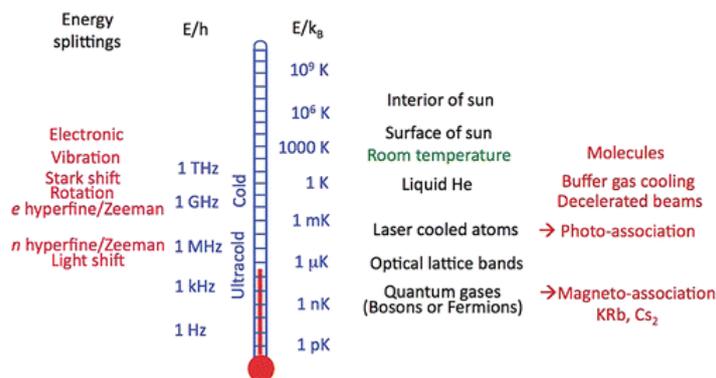
strategy. We also demonstrate for the first time that such analogues effectively induce latent HIV activation in vitro with potencies similar to or better than bryostatin. Significantly, these analogues are up to 1,000-fold more potent in inducing latent HIV expression than prostratin, the current clinical candidate for latent virus induction. This study provides the first demonstration that designed, synthetically accessible bryostatin analogues could serve as superior candidates for the eradication of HIV/AIDS through induction of latent viral reservoirs in conjunction with current antiretroviral therapy.

- Cosmic dust in the earth's atmosphere
Plane, J. M. C. *Chem. Soc. Rev.* **2012**, *41*, 6507-6518.
Abstract:



This review discusses the magnitude of the cosmic dust input into the earth's atmosphere, and the resulting impacts from around 100 km to the earth's surface. Zodiacal cloud observations and measurements made with a spaceborne dust detector indicate a daily mass input of interplanetary dust particles ranging from 100 to 300 tonnes, which is in agreement with the accumulation rates of cosmic-enriched elements (Ir, Pt, Os and super-paramagnetic Fe) in polar ice cores and deep-sea sediments. In contrast, measurements in the middle atmosphere – by radar, lidar, high-flying aircraft and satellite remote sensing – indicate that the input is between 5 and 50 tonnes per day. There are two reasons why this huge discrepancy matters. First, if the upper range of estimates is correct, then vertical transport in the middle atmosphere must be considerably faster than generally believed; whereas if the lower range is correct, then our understanding of dust evolution in the solar system, and transport from the middle atmosphere to the surface, will need substantial revision. Second, cosmic dust particles enter the atmosphere at high speeds and undergo significant ablation. The resulting metals injected into the atmosphere are involved in a diverse range of phenomena, including: the formation of layers of metal atoms and ions; the nucleation of noctilucent clouds, which are a sensitive marker of climate change; impacts on stratospheric aerosols and O₃ chemistry, which need to be considered against the background of a cooling stratosphere and geo-engineering plans to increase sulphate aerosol; and fertilization of the ocean with bio-available Fe, which has potential climate feedbacks.

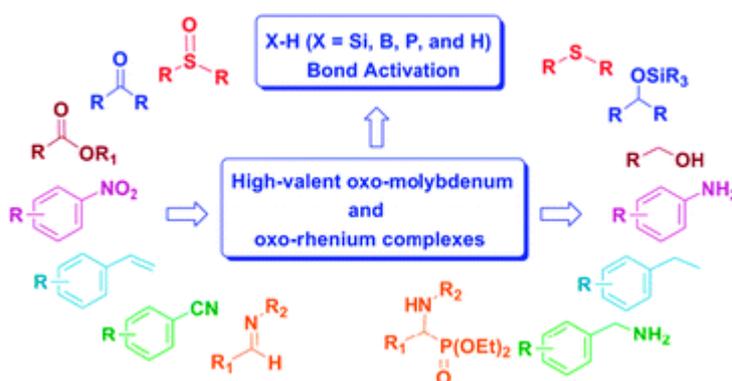
- Ultracold Molecules under Control!
Quéméner, G.; Julienne, P. S. *Chem. Rev.* **2012**, *112*, 4949-5011.

Abstract:

This review is concerned with the physics and chemistry associated with the interactions, collisions, and reactions of ultracold molecules, that is, molecules having translational temperatures on the order of μ K or less. Such molecules can now be produced in their rotational and vibrational ground states in the laboratory by using magnetic and electromagnetic control techniques to assemble them from already ultracold atoms. Theoretical tools are also being developed that are appropriate to this new regime. Chemists have to learn to think differently about the ultracold domain, which is on the order of 9 orders of magnitude removed from room temperature and even 6 orders of magnitude colder than the few K of interstellar space or liquid He. This enormous decrease in accessible temperature and entropy leads to new quantum phenomena and control possibilities. This review will cover the special aspects of this novel domain, including the essential features of the cooling and trapping of atoms and molecules, the magnetic, electric, and electromagnetic control techniques available for them, the formation of ultracold molecules, the ultracold collisions and reactions of molecules, and then end with some perspectives on the future of this rapidly developing new field. We will concentrate on the collisions and reactions of ultracold alkali molecules, especially polar molecules subject to electric field control.

- High-valent oxo-molybdenum and oxo-rhenium complexes as efficient catalysts for X–H (X = Si, B, P and H) bond activation and for organic reductions

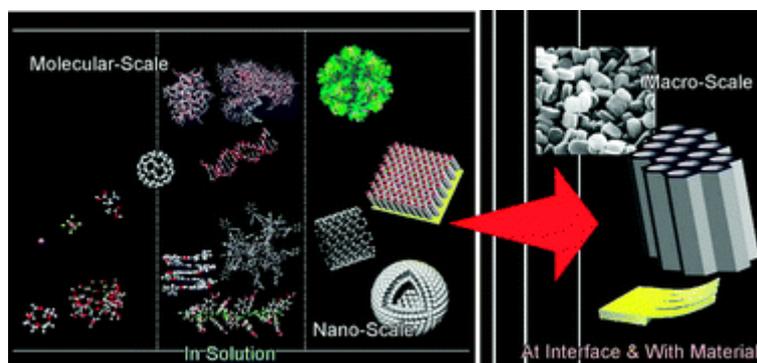
Sousa, S. C. A.; Cabrita, I.; Fernandes, A. C. *Chem. Soc. Rev.* **2012**, *41*, 5641-5653.

Abstract:

High-valent oxo-complexes have recently emerged as powerful catalysts for the activation of X–H (X = Si, B, P and H) bonds and for the reduction of several functional groups. This new reactivity represents a complete reversal from the traditional role of these complexes as oxidation catalysts and opened a new research area for high-valent oxo-complexes. This *tutorial review* highlights the work developed using high-valent oxo-molybdenum and oxo-rhenium complexes as excellent catalysts for X–H (X = Si, B, P and H) bond activation and for organic reductions.

- Molecular recognition: from solution science to nano/materials technology
Ariga, K.; Ito, H.; Hill, J. P.; Tsukube, H. *Chem. Soc. Rev.* **2012**, *41*, 5800-5835.

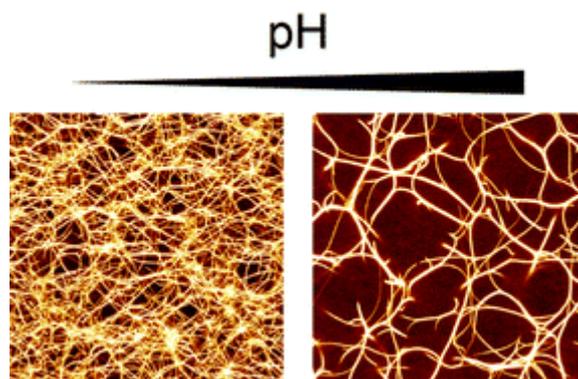
Abstract:



In the 25 years since its Nobel Prize in chemistry, supramolecular chemistry based on molecular recognition has been paid much attention in scientific and technological fields. Nanotechnology and the related areas seek breakthrough methods of nanofabrication based on rational organization through assembly of constituent molecules. Advanced biochemistry, medical applications, and environmental and energy technologies also depend on the importance of specific interactions between molecules. In those current fields, molecular recognition is now being re-evaluated. In this review, we re-examine current trends in molecular recognition from the viewpoint of the surrounding media, that is (i) the solution phase for development of basic science and molecular design advances; (ii) at nano/materials interfaces for emerging technologies and applications. The first section of this review includes molecular recognition frontiers, receptor design based on combinatorial approaches, organic capsule receptors, metallo-capsule receptors, helical receptors, dendrimer receptors, and the future design of receptor architectures. The following section summarizes topics related to molecular recognition at interfaces including fundamentals of molecular recognition, sensing and detection, structure formation, molecular machines, molecular recognition involving polymers and related materials, and molecular recognition processes in nanostructured materials.

- Modulation of cross-linked actin networks by pH
Schmoller, K. M.; Köhler, S.; Crevenna, A. H.; Wedlich-Söldner, R.; Bausch, A. R. *Soft Matter* **2012**, *8*, 9685-9690.

Abstract:

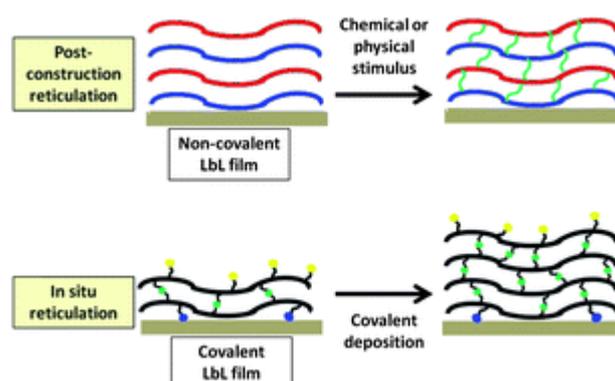


How cells orchestrate their complex cytoskeleton precisely in space and time is still far from understood. Recent studies suggest that local and transient variations of intracellular pH are critically involved in many important cytoskeletal processes. Yet, little is known about which proteins contribute to the pH sensitivity of cytoskeletal structures. Using macrorheology and confocal microscopy we investigate how a variation of pH affects structural and mechanical properties of reconstituted cross-linked actin systems. We demonstrate that each of the three cross-linking proteins tested here – cortaxillin, filamin and fascin – shows a distinctive pH dependence. Our results indicate that cross-linked actin structures constitute ideal targets for the generation of specific morphogenetic cellular responses by varying the intracellular pH. This also highlights the amazing flexibility and adaptability of a heterogeneous set of cytoskeletal structures in response to a single effect, such as the variation of pH.

- Strategies for covalently reticulated polymer multilayers

Rydzek, G.; Schaaf, P.; Voegel, J.-C.; Jerry, L.; Boulmedais, F. *Soft Matter* **2012**, *8*, 9738-9755.

Abstract:

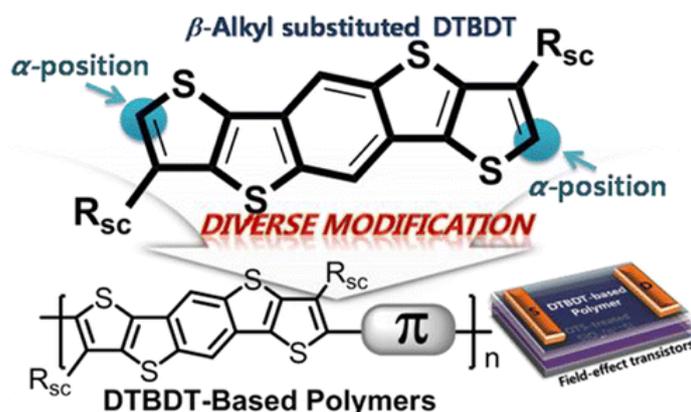


The past decade has seen a growing need for robust organic coating technologies in various fields going from biotechnology, sensing and electronic devices to membrane design. Polyelectrolyte multilayers constitute a major and versatile tool in this respect. Yet, these films usually suffer from chemical and mechanical weakness. Improvement of the chemical and mechanical stability of multilayer films can be brought about by covalent reticulation between the constituent polymers. Three main routes were developed for this purpose: post-reticulation after film buildup, step-by-step reticulation during film buildup and recently one-pot film construction. This review summarizes these main strategies with emphasis on the mechanisms of the chemical reactions used.

- β -Alkyl substituted Dithieno[2,3-d';3'-d']benzo[1,2-b;4,5-b']dithiophene Semiconducting Materials and Their Application to Solution-Processed Organic Transistors

Kim, J.; Han, A-R. Han; Jung, H. S.; Oh, J. H.; Yang, C. *Chem. Mater.* **2012**, *24*, 3464–3472.

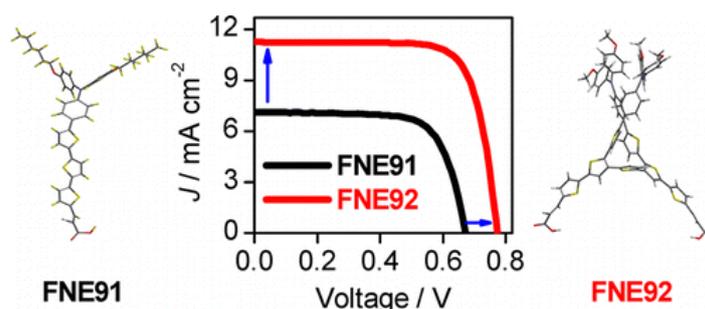
Abstract:



A novel highly π -extended heteroacene with four symmetrically fused thiophene-ring units and solubilizing substituents at the terminal β -positions on the central ring, dithieno[2,3-d';2',3'-d'']benzo[1,2-b;4,5-b']dithiophene (DTBDT) was synthesized via intramolecular electrophilic coupling reaction. The α -positions availability in the DTBDT motif enables the preparation of solution-processable DTBDT-based polymers such as PDTBDT, PDTBDT-BT, PDTBDT-DTBT, and PDTBDT-DTDP. Even with its highly extended acene-like π -framework, all polymers show fairly good environmental stability of their highest occupied molecular orbitals (HOMOs) from -5.21 to -5.59 eV. In the course of our study to assess a profile of semiconductor properties, field-effect transistor performance of the four DTBDT-containing copolymers via solution-process is characterized, and PDTBDT-DTDP exhibits the best electrical performance with a hole mobility of $1.70 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. PDTBDT-DTDP has a relatively smaller charge injection barrier for a hole from the gold electrodes and maintains good coplanarity of the polymer backbone, indicating the enhanced π - π stacking characteristic and charge carrier transport. The experimental results demonstrate that our molecular design strategy for air-stable, high-performance organic semiconductors is highly promising.

- Thiophene-Bridged Double D- π -A Dye for Efficient Dye-Sensitized Solar Cell
Ren, X.; Jiang, S.; Cha, M.; Zhou, G.; Wang, Z.-S. *Chem. Mater.* **2012**, *24*, 3493–3499.

Abstract:



An organic dye containing two D- π -A branches linked with a thiophene unit has been designed and synthesized for efficient dye-sensitized solar cells (DSSCs). As compared to the rod-shape of the single D- π -A analogue dye, the cross shape of the double D- π -A branched dye is favorable for reducing intermolecular interaction and retarding charge recombination. Controlled intensity modulated photovoltage spectroscopy reveals that electron lifetime for the double D- π -A dye-based DSSC is 14-fold longer than that for the corresponding single D- π -A dye-based DSSC. Linking two D- π -A branches with a thiophene unit increases open-circuit photovoltage by 100 mV and short-circuit photocurrent by 4.10 mA cm^{-2} . As a consequence, power conversion efficiency is enhanced by about 2-fold. This work presents a new route to designing sensitizers with high suppression ability of charge recombination toward high-performance DSSCs.