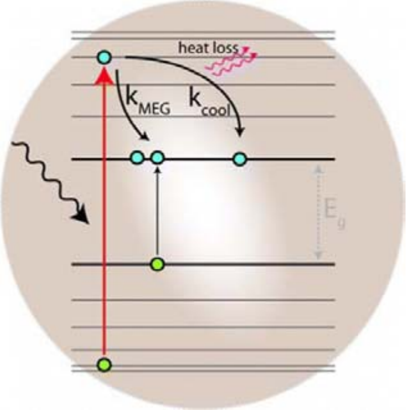
- Third Generation Photovoltaics based on Multiple Exciton Generation in Quantum Confined Semiconductors
  Beard, M. C.; Luther, J. M.; Semonin, O. E.; Nozik, A. J. *Acc. Chem. Res.* **2013**, *46*, 1252–1260.
  Abstract:



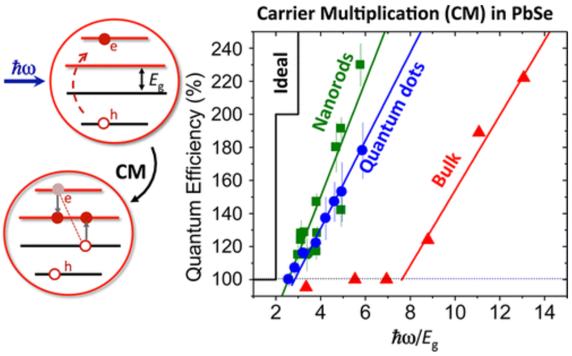
Improving the primary photoconversion process in a photovoltaiccell by utilizing the excess energy that is otherwise lost as heat can lead to an increase in the overall power conversion efficiency (PCE). Semiconductor nanocrystals (NCs) with at least one dimension small enough to produce quantum confinement effects provide new ways of controlling energy flow not achievable in thin film or bulk semiconductors. Researchers have developed various strategies to incorporate these novel structures into suitable solar conversion systems. Some of these methods could increase the PCE past the Shockley–Queisser (SQ) limit of ~33%, making them viable “third generation photovoltaic” (TGPV) cell architectures. Surpassing the SQ limit for single junction solar cells presents both a scientific and a technological challenge, and the use of semiconductor NCs to enhance the primary photoconversion process offers a promising potential solution.

The NCs are synthesized via solution phase chemical reactions prod-ucing stable colloidal solutions, where the reaction conditions can be modified to produce a variety of shapes, compositions, and structures. The confinement of the semiconductor NC in one dimension produces quantum films, wells, or discs. Two-dimensional confinement leads to quantum wires or rods (QRs), and quantum dots (QDs) are three-dimensionally confined NCs. The process of multiple exciton generation (MEG) converts a high-energy photon into multiple electron–hole pairs. Although many studies have demonstrated that MEG is enhanced in QDs compared with bulk semiconductors, these studies have either used ultrafast spectroscopy to measure the photon-to-exciton quantum yields (QYs) or theoretical calculations. Implementing MEG in a working solar cell has been an ongoing challenge.

In this Account, we discuss the status of MEG research and strategies towards implementing MEG in working solar cells. Recently we showed an external quantum efficiency for photocurrent of greater than 100% (reaching 114%) at ~$4E_g$ in a PbSe QD solar cell. The internal quantum efficiency reached 130%. These results compare favorably with ultrafast transient spectroscopic measurements. Thus, we have shown that one of the tenets of the SQ limit, that photons only produce one electron–hole pair at the electrodes of a solar cell, can be overcome. Further challenges include increasing the MEG efficiency and improving the QD device structure and operation.

- Carrier Multiplication in Semiconductor Nanocrystals: Influence of Size, Shape, and Composition
  Padilha, L. A.; Stewart, J. T.; Sandberg, R. L.; Bae, W. K.; Koh, W.-K.; Pietryga, J. M.; Klimov, V. I. *Acc. Chem. Res.* **2013**, *46*, 1261–1269.

Abstract:



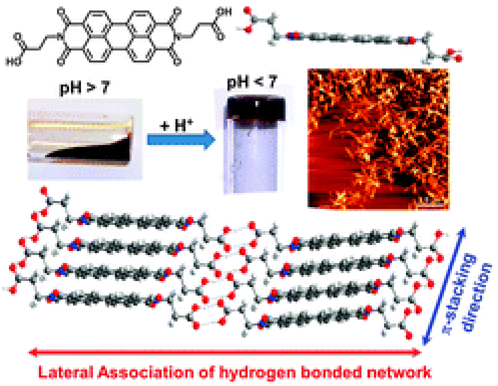
During carrier multiplication (CM), also known as multiexciton generation (MEG), absorption of a single photon produces multiple electron-hole pairs, or excitons. This process can appreciably increase the efficiency of photoconversion, which is especially beneficial in photocatalysis and photovoltaics.

This Account reviews recent progress in understanding the CM process in semiconductor nanocrystals (NCs), motivated by the challenge researchers face to quickly identify candidate nanomaterials with enhanced CM. We present a possible solution to this problem by showing that, using measured biexciton Auger lifetimes and intraband relaxation rates as surrogates for, respectively, CM time constants and non-CM energy-loss rates, we can predict relative changes in CM yields as a function of composition. Indeed, by studying PbS, PbSe, and PbTe NCs of a variety of sizes we determine that the significant difference in CM yields for these compounds comes from the dissimilarities in their non-CM relaxation channels, i.e., the processes that compete with CM. This finding is likely general, as previous observations of a material-independent, “universal” volume-scaling of Auger lifetimes suggest that the timescale of the CM process itself is only weakly affected by NC composition.

We further explore the role of nanostructure shape in the CM process. We observe that a moderate elongation (aspect ratio of 6–7) of PbSe NCs can cause up to an approximately two-fold increase in the multiexciton yield compared to spherical nanoparticles. The increased Auger lifetimes and improved charge transport properties generally associated with elongated nanostructures suggest that lead chalcogenide nanorods are a promising system for testing CM concepts in practical photovoltaics.

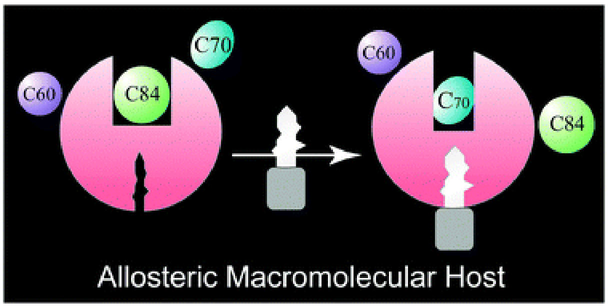
Historically, experimental considerations have been an important factor influencing CM studies. To this end, we discuss the role of NC photocharging in CM measurements. Photocharging can distort multiexciton dynamics, leading to erroneous estimations of the CM yield. Here, we show that in addition to distorting time-resolved CM signals, photocharging also creates spectral signatures that mimic CM. This re-emphasizes the importance of a careful analysis of the potential effect of charged species in both optical and photocurrent-based measurements of this process.

- One-dimensional self-assembly of a water soluble perylene diimide molecule by pH triggered hydrogelation
  Datar, A.; Balakrishnanab, K.; Zang, L. *Chem. Commun*. **2013**, *49*, 6894-6896.
  Abstract:



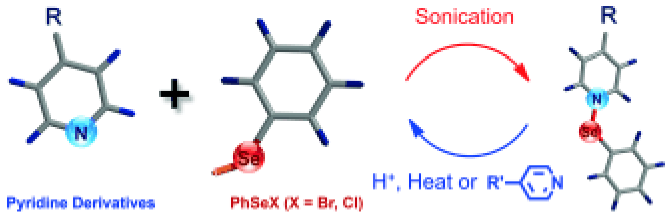
A water soluble perylene diimide molecule has been fabricated into nanofibers via a pH triggered hydrogelation route. The one-dimensional self-assembly is dominated by the intermolecular π–π stacking interactions in concert with the hydrogen bonding between the carboxylic acid side chains. The anisotropic electronic and optical properties observed for the nanofibers are consistent with the one-dimensional intermolecular π–π arrangement.

- Dynamic control of dendrimer–fullerene association by axial coordination to the core
  Albrecht, K.; Kasai, Y.; Kuramotoa, Y.; Yamamoto, K. *Chem. Commun*. **2013**, *49*, 6861-6863.
  Abstract:



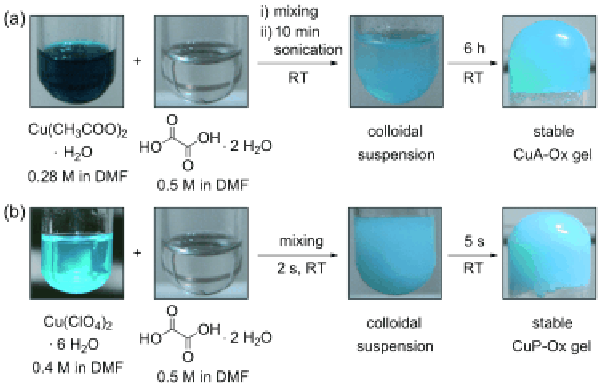
The effect of axial coordination of pyridine derivatives to the core porphyrin on the fullerene encapsulation of the 4th generation carbazole–phenylazomethine dendrimer (ZnPG2-2) was investigated. The axial coordination of large (bulky) pyridine derivatives affects the cavity in an allosteric manner, and the size-selectivity of the fullerene association could be controlled.

- A New Dynamic Covalent Bond of Se—N: Towards Controlled Self-Assembly and Disassembly
  Yi, Y.; Xu, H.; Wang, L.; Cao, W.; Zhang, X. *Chem. Eur. J.* **2013**, *29*, 9506-9510.
  Abstract:



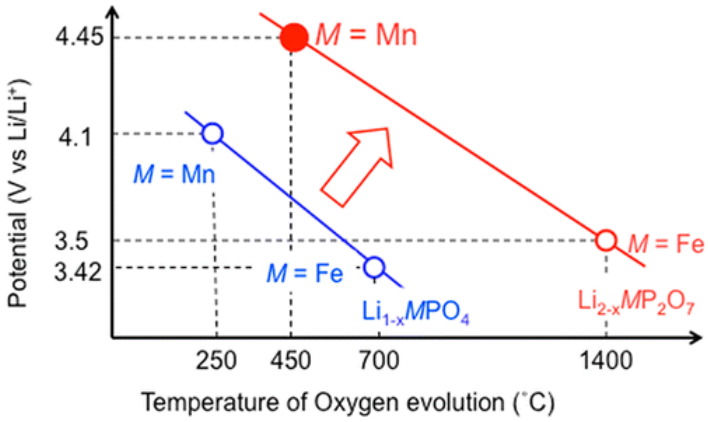
A new kind of Se—N dynamic covalent bond has been found that can form between the Se atom of a phenylselenyl halogen species and the N atom of a pyridine derivative, such as polystyrene-b-poly(4-vinylpyridine). This Se—N dynamic covalent bond can be reversibly and rapidly formed or cleaved under acidic or basic conditions, respectively. Furthermore, the bond can be dynamically cleaved by heating or treatment with stronger electron-donating pyridine derivatives. The multiple responses of Se—N bond to external stimuli has enriched the existing family of dynamic covalent bonds. It can be used for controlled and reversible self-assembly and disassembly, which may find potential applications in a number of areas, including self-healing materials and responsive assemblies.

- Proton-Conducting Supramolecular Metallogels from the Lowest Molecular Weight Assembler Ligand: A Quote for Simplicity
  Saha, S.; Schön, E.-M.; Cativiela, C.; Díaz, D. ; Banerjee, R. *Chem. Eur. J.* **2013**, *29*, 9562-9568.
  Abstract:



Oxalic acid has been proven to be the lowest molecular weight organic ligand able to form robust supramolecular metallogel networks in the presence of metal salts. In particular, two novel multifunctional metallogels were readily prepared at room temperature by simple mixing of stock solutions of Cu^{II} acetate monohydrate or Cu^{II} perchlorate hexahydrate and oxalic acid dihydrate. Formation of different polymorphs and unprecedented proton conduction under anhydrous conditions were also demonstrated with some of these materials.

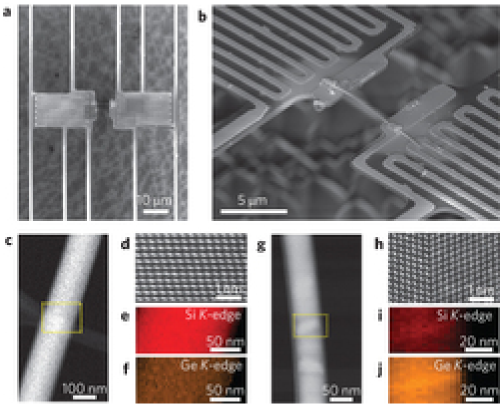
- Pyrophosphate Chemistry toward Safe Rechargeable Batteries
  Tamaru, M.; Chung, S. C.; Shimizu, D.; Nishimura, S.; Yamada, A. *Chem. Mater.* **2013**, *25*, 2538-2543.
  Abstract:



We demonstrate that pyrophosphate anion can result in metal pyrophosphate cathode materials with high thermal stabilities. High temperature behaviors for the delithiated states of $Li_2FeP_2O_7$ and $Li_2MnP_2O_7$ in the $P2_1/c$ symmetry are studied. Above 540 °C, the singly delithiated structure $LiFeP_2O_7$ undergoes an irreversible phase transformation to the ground state polymorph with a symmetry of $P2_1$. Intermediate delithiated compounds $Li_{2-x}FeP_2O_7$ ($0 < x < 1$) convert to a mixture of $LiFeP_2O_7$ in the

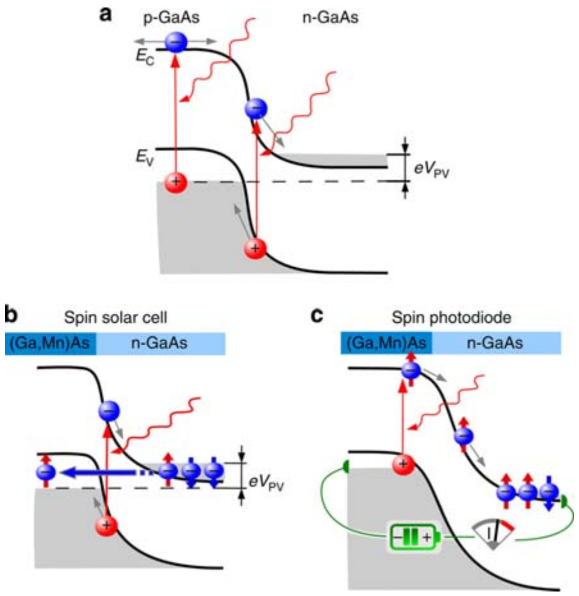
P2_1 symmetry and $Li_2FeP_2O_7$ in the *P*2_1/*c* symmetry. No decomposition is observed for both the singly and partially delithiated compounds until 600 °C showing the high thermal stabilities of the compounds. Analysis of phase stabilities reveals that $LiFeP_2O_7$ (*P*2_1/*c*) is intrinsically more stable than $FePO_4$ (olivine) against reduction (high temperature). Similar high thermal stability is also observed for $Li_{1.4}MnP_2O_7$. It decomposes to $Li_2MnP_2O_7$, $Mn_2P_2O_7$, $LiPO_3$, and O_2 at 450 °C, much higher than the olivine counterpart $MnPO_4$. The high stability of these metal pyrophosphates is rationalized by the stability of the $P_2O_7^{4-}$ anion.

- Observation of room-temperature ballistic thermal conduction persisting over 8.3 µm in SiGe nanowires
  Hsiao, T.-K.; Chang, H.-K.; Liou, S.-C.; Chu, M.-W.; Lee, S.-C.; Chang, C.-W. *Nature Nano.* **2013**, *8*, 534–538.
  Abstract:



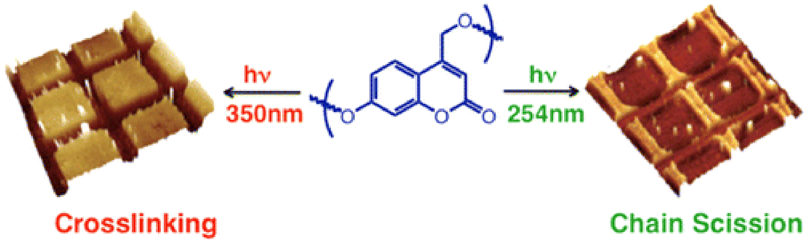
In ballistic thermal conduction, the wave characteristics of phonons allow the transmission of energy without dissipation. However, the observation of ballistic heat transport at room temperature is challenging because of the short phonon mean free path. Here we show that ballistic thermal conduction persisting over 8.3 µm can be observed in SiGe nanowires with low thermal conductivity for a wide range of structural variations and alloy concentrations. We find that an unexpectedly low percentage (~0.04%) of phonons carry out the heat conduction process in SiGe nanowires, and that the ballistic phonons display properties including non-additive thermal resistances in series, unconventional contact thermal resistance, and unusual robustness against external perturbations. These results, obtained in a model semiconductor, could enable wave-engineering of phonons and help to realize heat waveguides, terahertz phononic crystals and quantum phononic/thermoelectric devices ready to be integrated into existing silicon-based electronics

- Demonstration of the spin solar cell and spin photodiode effect
  Endres, B.; Ciorga, M.; Schmid, M.; Utz, M.; Bougeard, D.; Weiss, D.; Bayreuther, G.; Back, C. H. *Nat Commun* **2013**, *4*, 2068.
  Abstract:



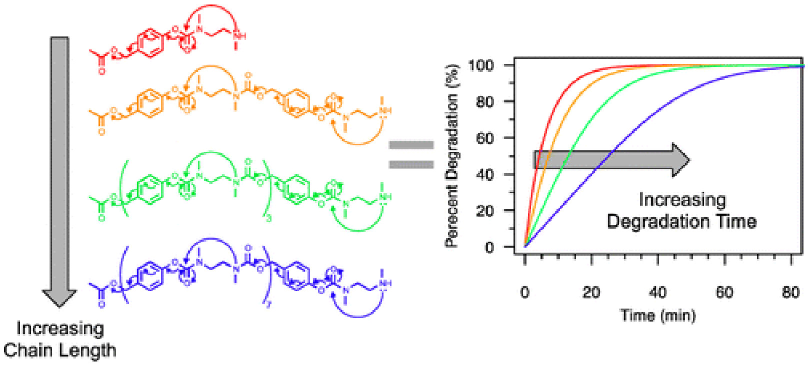
Spin injection and extraction are at the core of semiconductor spintronics. Electrical injection is one method of choice for the creation of a sizeable spin polarization in a semiconductor, requiring especially tailored tunnel or Schottky barriers. Alternatively, optical orientation can be used to generate spins in semiconductors with significant spin-orbit interaction, if optical selection rules are obeyed, typically by using circularly polarized light at a well-defined wavelength. Here we introduce a novel concept for spin injection/extraction that combines the principle of a solar cell with the creation of spin accumulation. We demonstrate that efficient optical spin injection can be achieved with unpolarized light by illuminating a p-n junction where the p-type region consists of a ferromagnet. The discovered mechanism opens the window for the optical generation of a sizeable spin accumulation also in semiconductors without direct band gap such as Si or Ge.

- Photoresponsive Coumarin Polyesters That Exhibit Cross-Linking and Chain Scission Properties
  Maddipatla, M.V. S. N.; Wehrung, D.; Tang, C.; Fan, W.; Oyewumi, M. O.; Miyoshi, T.; Joy, A.
  Macromolecules **2013**, *46*, 5133-5140.
  Abstract:



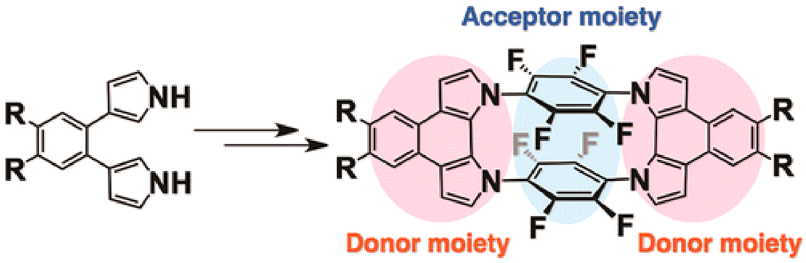
The synthesis and properties of a new class of photoresponsive coumarin polyesters are described. Incorporation of the coumarin chromophore in the polymer chain provides interesting properties such as polymer chain cross-linking upon irradiation at 350 nm and chain un-cross-linking when irradiated at 254 nm. In addition, irradiation at 254 nm also results in polymer chain scission. The cross-linking, un-cross-linking, and chain scission properties were studied by ssNMR, ATR-IR, and GPC measurements. These properties enable the fabrication of 2D surfaces having complementary micropatterned features. Also, initial biocompatibility profiles of the polymers and their irradiation products were demonstrated using MTT assays.

- Kinetics of Self-Immolative Degradation in a Linear Polymeric System: Demonstrating the Effect of Chain Length
  McBride, R. A.; Gillies, E. R. *Macromolecules* **2013**, *46*, 5157-5166.
  Abstract:



We describe here a study demonstrating that the degradation time of self-immolative linear polymers is dependent on chain length. These materials are unique relative to most degradable polymers, in that they undergo end-to-end depolymerization in response to the cleavage of an end-cap. Although one of their cited attributes is a dependence of their degradation time on chain length, no conclusive study has been conducted to demonstrate and study this effect. In this work, using a linear self-immolative polymer backbone derived from alternating 4-hydroxybenzyl alcohol and N,N′-dimethylethylenediamine based spacers, we show that there is a proportional relationship between chain length and depolymerization time. This is first accomplished using a series of oligomers synthesized using a convergent, iterative route and then applied to the polydisperse case on a set of polymers displaying varying molecular weights. We also report the first development and validation of a self-immolative degradation model relating monomer kinetics to polymer degradation and show its application in explaining oligomeric and polymeric degradation profiles.

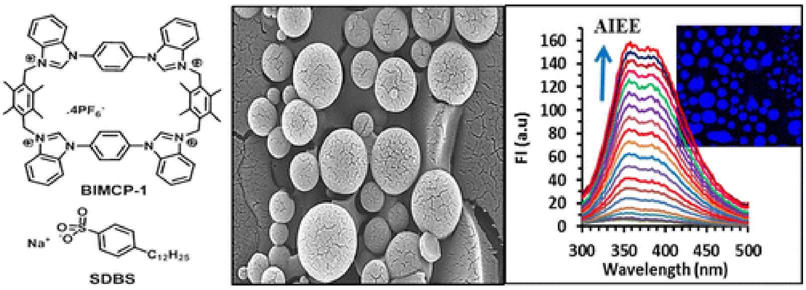
- Donor–Acceptor Segregated Paracyclophanes Composed of Naphthobipyrrole and Stacked Fluoroarenes
  Takase, M.; Inabe, A.; Sugawara, Y.; Fujita, W.; Nishinaga, T.; Nomura, K. *Org. Lett.* **2013**, *15,* 3202-3205.
  Abstract:



The expeditious synthesis of donoracceptor segregated paracyclophanes has been achieved by a selective SNAr reaction of hexafluorobenzene with o-dipyrrolylbenzenes and subsequent cyclodehydrogenation. An orthogonally arranged DA segregated structure was confirmed by X-ray crystallography. The combined results of DFT calculations and absorption spectra revealed the charge transfer (CT) nature from the naphthobipyrrole (donor) to the stacked fluoroarene moiety (acceptor).

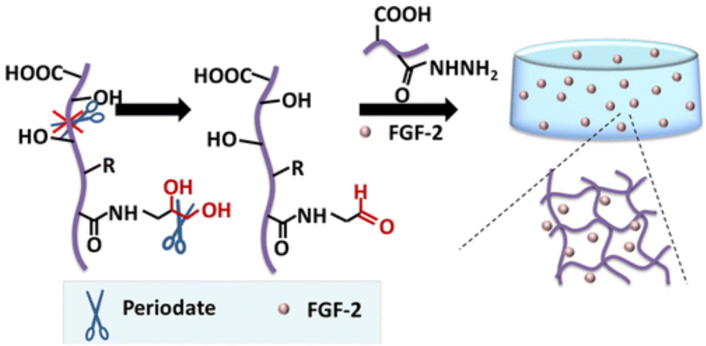
- Aggregation Induced Emission Enhancement in Ionic Self-Assembled Aggregates of Benzimidazolium Based Cyclophane and Sodium Dodecylbenzenesulfonate

Kumar, S.; Singh, P.; Mahajan, A.; Kumar, S. *Org. Lett.* **2013***, 15,* 3400-3403.
<u>Abstract:</u>



Cyclophane BIMCP-1 undergoes ionic self-assembly with surfactant sodium dodecylbenzenesulfonate (SDBS) at a concentration far below its CMC value to form aggregates with spherical morphology. The rotational restriction of rings in these aggregates facilitates 32-fold enhancement in emission intensity (AIEE) to allow fluorescence based determination of SDBS with 4 µM (1.4 ppm) as the lowest detection limit. Sodium salts of fatty acids and inorganic anions halides, CN$^-$, HSO$_4^-$, SO$_4^{2-}$, H$_2$PO$_4^-$, SCN$^-$ and NO$_3^-$ do not interfere in the estimation of SDBS.

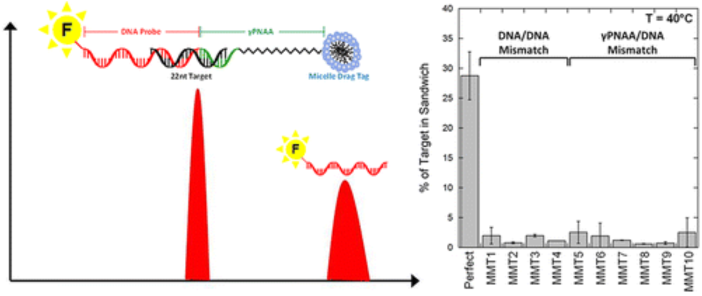
- Mild and Efficient Strategy for Site-Selective Aldehyde Modification of Glycosaminoglycans: Tailoring Hydrogels with Tunable Release of Growth Factor
  Wang, S.; Oommen, O. P.; Yan, H.; Varghese, O. P. *Biomacromolecules* **2013**, *14*, 2427-2432.
  <u>Abstract:</u>



Aldehydes have been used as an important bioorthogonal chemical reporter for conjugation of large polymers and bioactive substances. However, generating aldehyde functionality on carbohydrate-based biopolymers without changing its native chemical structure has always persisted as a challenging task. The common methods employed to achieve this require harsh reaction conditions, which often compromise the structural integrity and biological function of these sensitive molecules. Here we report a mild and simple method to graft aldehydes groups on glycosaminoglycans (GAGs) in a site-selective manner without compromising the structural integrity of the biopolymer. This regio-selective modification was achieved by conjugating the amino-glycerol moiety on the carboxylate residue of the polymer, which allowed selective cleavage of pendent diol groups without interfering with the C2–C3 diol groups of the native glucopyranose residue. Kinetic evaluation of this reaction demonstrated significant differences in second-order reaction rate for periodate oxidation (by four-orders of magnitude) between the two types of vicinal diols. We employed this chemistry to develop aldehyde modifications of sulfated and nonsulfated GAGs such as hyaluronic acid (HA), heparin (HP), and chondroitin sulfate (CS). We further utilized these aldehyde grafted GAGs to tailor extracellular matrix mimetic injectable hydrogels and evaluated its rheological properties. The composition of the hydrogels was also found to modulate release of therapeutic protein such as FGF-2, demonstrating

controlled release (60%) for over 14 days. In short, our result clearly demonstrates a versatile strategy to graft aldehyde groups on sensitive biopolymers under mild conditions that could be applied for various bioconjugation and biomedical applications such as drug delivery and regenerative medicine.

- High Affinity γPNA Sandwich Hybridization Assay for Rapid Detection of Short Nucleic Acid Targets with Single Mismatch Discrimination
  Goldman, J. M.; Zhang, L. A.; Manna, A.; Armitage, B. A.; Ly, D. H.; Schneider, J. W. *Biomacromolecules* **2013**, *14*, 2253-2261.
  Abstract:



Hybridization analysis of short DNA and RNA targets presents many challenges for detection. The commonly employed sandwich hybridization approach cannot be implemented for these short targets due to insufficient probe-target binding strengths for unmodified DNA probes. Here, we present a method capable of rapid and stable sandwich hybridization detection for 22 nucleotide DNA and RNA targets. Stable hybridization is achieved using an *n*-alkylated, polyethylene glycol γ-carbon modified peptide nucleic acid (γPNA) amphiphile. The γPNA's exceptionally high affinity enables stable hybridization of a second DNA-based probe to the remaining bases of the short target. Upon hybridization of both probes, an electrophoretic mobility shift is measured via interaction of the *n*-alkane modification on the γPNA with capillary electrophoresis running buffer containing nonionic surfactant micelles. We find that sandwich hybridization of both probes is stable under multiple binding configurations and demonstrate single base mismatch discrimination. The binding strength of both probes is also stabilized via coaxial stacking on adjacent hybridization to targets. We conclude with a discussion on the implementation of the proposed sandwich hybridization assay as a high-throughput microRNA detection method.