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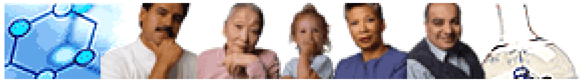

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# Heart Cut

**April 3, 2006**

- Anthracene-based oligomers as organic semiconductors
- Template-derived amine-functionalized siloxane nanocages
- Use quantum dots as light-harvesting “antennae”
- Ionic-liquid micelles of poly(1,2-butadiene-*b*-ethylene oxide)
- Gold–platinum catalysts have dendritic nanostructures
- Semiconductor microcapsules from polymer templates
- Change reaction solvent to reject impurities during workup
- Stereoselective synthesis of unsaturated carboxylic acids

Patent Watch
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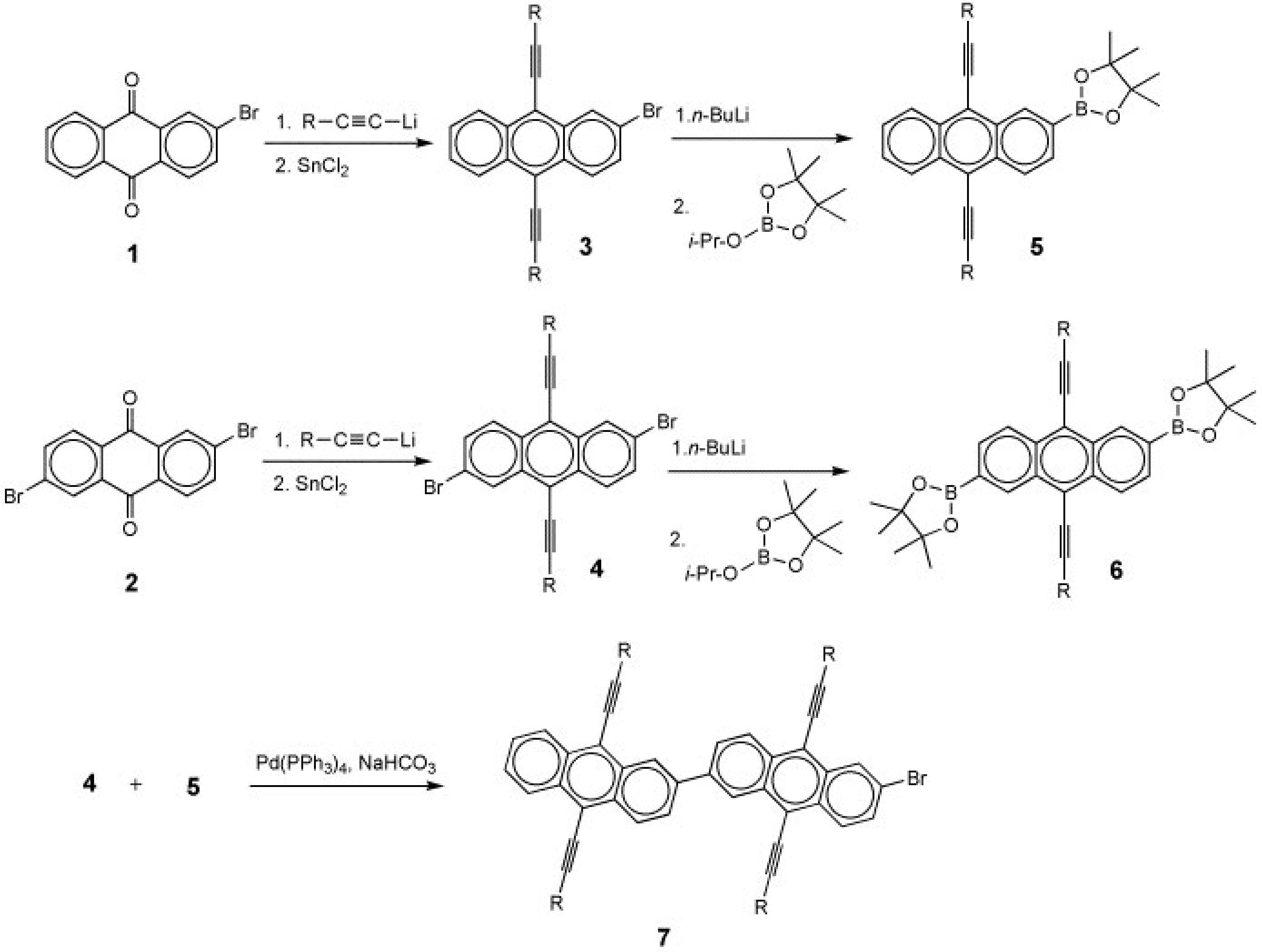
**These 9,10-bisalkynylanthrylene oligomers may be useful as organic semiconductors.** Anthracene is one of the most important fused-ring aromatic structures for optoelectronic devices. It has a charge carrier mobility as high as 3 $cm^2/(V \cdot s)$ in single crystals at room temperature. Y. Geng and co-workers at the Chinese Academy of Sciences (Changchun) reasoned that monodisperse conjugated oligomers based on anthracene would have significant potential for flexible optoelectronic devices.

Using Suzuki coupling reaction, they developed a synthesis for anthracene-based oligomers with as many as five anthracene units. The synthesis for the pentamer is shown below.


Br
O
O
1
1. R−C≡C−Li
2. SnCl$_2$
R
R
Br
3
1. n-BuLi
2.
i-Pr-O
B
O
O
R
R
B
O
O
5
Br
Br
O
O
2
1. R−C≡C−Li
2. SnCl$_2$
Br
Br
R
R
4
1. n-BuLi
2.
i-Pr-O
B
O
O
R
R
B
O
O
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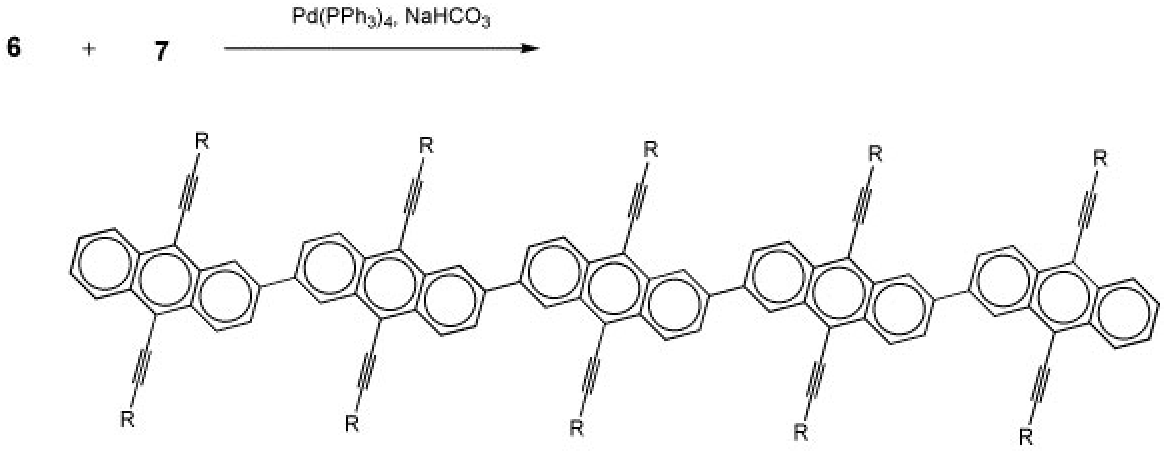
R
R
R
R
Br
7



**8**

Starting brominated anthraquinones **1** and **2** were available via the Sandmeyer reaction of their respective aminoanthraquinones. This was followed by treatment with the desired alkyl-substituted alkynyllithium reagent to insert the conjugated alkynyl groups. The anthracene core was then formed by deoxygenation with $SnCl_2$ to give intermediates **3** and **4**.

To set the stage for the coupling reaction, **3** and **4** were activated with *n*-BuLi and treated with a dioxaborolane. The resulting mono- and bisboronates, **5** and **6**, formed under very mild conditions. Suzuki coupling of **4** and **5**, also under mild conditions (THF reflux), provided the key brominated dimer **7**, which was subjected to a second coupling with bisboronate **6** to give target pentamer **8** in 54% yield.

Pentamer **8** with R = $C_6H_{13}$ had limited solubility in common organic solvents. However, replacing $C_6H_{13}$ with $C_8H_{17}$ in some of the repeat units provided enough solubility in $CHC_{l3}$ to prepare spin-coated films.

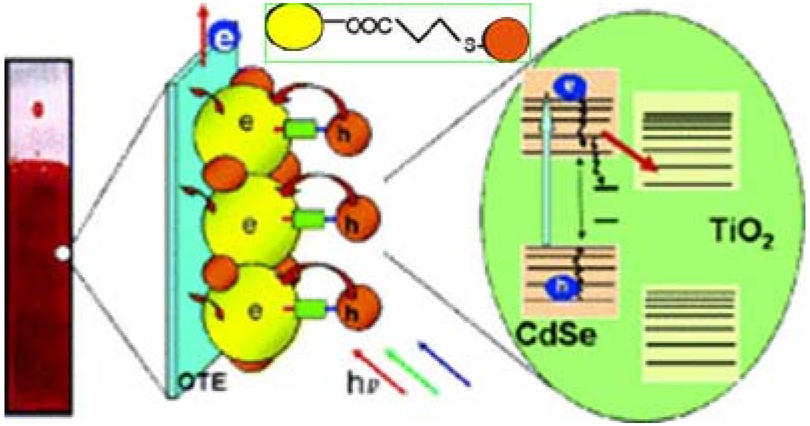
X-ray diffraction studies of single crystals showed that each anthracene unit is coplanar with at least one pair of alkynyl chains, which the authors believe is favorable for the close intermolecular packing of the oligomers necessary for good charge carrier transport in the solid state. The authors prepared a thin film field-effect transistor from the pentamer, and calculated a field-effect mobility of 2.95 x $10^{-3}$ $cm^2/(V \cdot s)$. (*Org. Lett.* **2006,** *8,* 785－788; W. Jerry Patterson) Go to top

**Produce amine-functionalized siloxane nanocages using a carbamate surfactant template.** H. H. Kung and co-workers at Northwestern University (Evanston, IL) used cetyl *N*-[3-(triethoxysilyl)propyl]carbamate as a template surfactant capable of forming nanometer-sized micelles in EtOH. Hydrolyzing the siloxy headgroups in acidic EtOH－$H_2O$ resulted in cross-linking the ~2-nm particles, which could then be further cross-linked and end-capped with reactive silanes. Physically robust shell cross-linked micelles (SCMs) were produced in this manner.

Cleaving the carbamate bonds in the SCMs with $Me_3SiI$ produced siloxane nanocages functionalized with tethered amino groups. The 2-nm particle size was retained during this conversion. The nanocages are porous and can bind to materials that contain amino-group receptors, such as zinc tetraphenylporphyrin. The authors propose that altering the length of the hydrophobic tails could similarly produce nanocages of different diameters. (*J. Am. Chem. Soc.* **2006,** *128,* 2776－2777; David A. Schiraldi) Go to top

**Use quantum dots as light-harvesting “antennae”.** Ordered assemblies of semiconductor nanoparticles with narrow band gaps have been used to harvest visible light energy in photoelectrochemical cells. However, the photocurrents obtained from these assembly systems are often low because fast charge recombination limits photocurrent generation.

M. Kuno, P. V. Kamat, and co-workers at the University of Notre Dame (IN) have prepared a semiconductor heterojunction structure by linking two kinds of nanoparticles with tailored band offsets through a group of bifunctional surface modifiers. This assembly exhibits high photon-to-charge carrier generation efficiency.



CdSe quantum dots (average ~4 nm diam; shown in orange) were assembled onto mesoporous films of TiO$_2$ nanoparticles (average ~50 nm diam; yellow) with the aid of bifunctional surface modifiers (green). In this case, the modifier was $HSCH_2CH_2CO_2H$. Upon visible-light excitation, the CdSe nanodots inject electrons from their conduction bands into the TiO$_2$ nanoparticles with rates of 7.3 – 195 x 10$^9$ s$^{-1}$. When the CdSe – TiO$_2$ nanocomposite is used as a photoanode in a photocell, it exhibits a photocurrent generation efficiency as high as 12%. (*J. Am. Chem. Soc.* **2006,** *128,* 2385 – 2393; Ben Zhong Tang) Go to top

**Poly(1,2-butadiene-*b*-ethylene oxide) self-assembles in an ionic liquid.** T. P. Lodge and co-workers at the University of Minnesota (Minneapolis) studied the micellization of block copolymers of butadiene and ethylene oxide in an ionic liquid at room temperature. They prepared four poly(1,2-butadiene-*b*-ethylene oxide) (PB-*b*-PEO) copolymers with different PEO block lengths. In a “PEO-friendly” ionic solvent, 1-butyl-3-methylimidazolium hexafluorophosphate, microphase separation occurred with PB as the core and the PEO block as the corona. Spherical micelles, wormlike micelles, and bilayered vesicles were formed as the PEO fraction was decreased from 64 to 25 vol%. When the PEO fraction was <40 vol%, multiple morphologies coexisted.

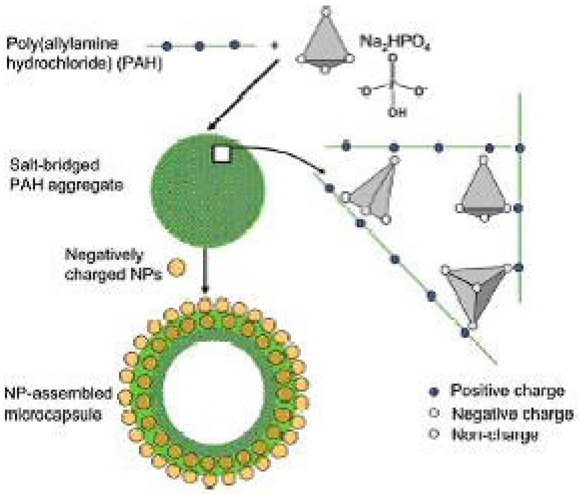
Cryogenic transmission electron microscopy (cryo-TEM) and dynamic light scattering (DLS) techniques were used to measure the micelle dimensions. The spherical micelle radii determined by cryo-TEM were very close to the hydrodynamic radius values measured by DLS. Micelle sizes were not affected by raising the temperature from 25 to 100 ° C. (*J. Am. Chem. Soc.* **2006,** *128,* 2745−2750; Sally Peng Li) Go to top

**These gold – platinum catalysts have dendritic heteroaggregate nanostructures.** The catalytic behavior of bimetallic catalyst systems in electrochemical fuel cells depends on the nanoparticle (NP) architecture. According to B. Eichhorn and coauthors at the University of Maryland (College Park) and Hitachi Instruments (Pleasanton, CA), a novel Au – Pt catalyst with a dendritic heteroaggregate nanostructure shows very high selectivity for CO oxidation and high hydrogen thermal oxidation activity <100 ° C in mixed CO – H$_2$ fuel streams.

Monometallic 5-nm platinum-colloid and 11-nm gold-colloid NPs were used as the unit blocks for assembling the Au－Pt heteroaggregate nanostructure via a modified core－shell particle growth pathway. Platinum “grows” from the gold “seed” as dendritic tendrils (7 nm diam) to form the heteroaggregate structure. The nonalloyed gold and platinum phases play a central role in catalytic performance, which is enhanced by their tolerance for CO.

The authors believe that because CO does not bind strongly to the large gold NPs, the gold core can activate oxygen and facilitate CO oxidation at the Au－Pt interface (the triple-phase boundary). Compared with standard Pt－Ru catalyst systems, this Pt－Au catalyst may be an excellent candidate for low-temperature anode electrocatalysts in fuel-cell applications. (*J. Am. Chem. Soc.* **2006,** *128,* 1780－1781; George Xiu Song Zhao) Go to top

**Semiconductor microcapsules can assemble around polymer aggregate templates.** M. S. Wong and co-workers at Rice University (Houston) prepared semiconductor microcapsules of $SnO_2$ particles that were assembled using poly(allylamine hydrochloride) (PAH) and $NaHPO_4$. In the first step, a cationic polymer solution of PAH was treated with $NaHPO_4$ to form aggregates, as shown in the figure.

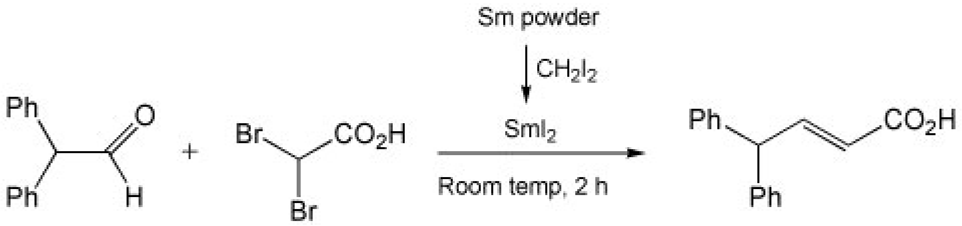


Combining the aggregates with spherical $SnO_2$ particles (0.5－3 μm diam) formed a multilayer thick shell that was held together by negative charges on the nanoparticles and positive charges on the PAH. The authors refer to this process as “polymer-aggregate templating”. The overall diameter of the microcapsules doubled when aging time was increased from 2 to 30 min. The microcapsules exhibited the same nanoscale optical properties as the starting tin oxide particles. (*Chem. Commun.* **2006,** 1097－1099; David A. Schiraldi) Go to top

**Change the reaction solvent to reject impurities during workup and improve the overall yield.** The reaction of 7-hydroxyisoquinoline with $(CF_3SO_2)_2O$ in EtOAc－pyridine gave the desired triflate in 48% yield after aqueous workup followed by high-vacuum distillation on a thin-film evaporator. Material was lost because the desired product reacted with the ethylene glycol ether used as a lubricant during distillation to solubilize pyridinium salt residues.

M. Bänziger, N. Yusuff, and co-workers at Novartis (Basel, Switzerland, and Cambridge, MA) replaced EtOAc with *t*-BuOMe, permitting more efficient removal of pyridinium salts. The amount of lubricant and the distillation temperature could be lowered significantly and the yield improved to 75－85%. (*Org. Process Res. Dev.* **2006,** *10,* 70－77; Will Watson) Go to top

**Use samarium diiodide to synthesize unsaturated carboxylic acids stereoselectively.** J. M. Concellón* and C. Concellón at the University of Oviedo (Spain) report the $SmI_2$-mediated reaction of aldehydes with $CHBr_2CO_2H$ to provide (*E*)-α,β-unsaturated carboxylic acids with complete stereoselectivity. To produce this remarkably efficient synthesis, the authors added $CH_2I_2$ to a suspension of samarium powder, $CHBr_2CO_2H$, and the aldehyde to generate $SmI_2$ in situ. The mixture was stirred 2 h at room temperature and quenched with aqueous HCl. The product was extracted with $CH_2Cl_2$.



Various aliphatic aldehydes were used in this study. Product yields varied from 76 to 93%, with de > 98% in every case. The authors noted that the reaction proceeds smoothly under mild conditions, with no need for protection and subsequent deprotection of the carboxylic acid group, and it uses commercially available reactants. (*J. Org. Chem.* **2006,** *71,* 1728－1731; W. Jerry Patterson) Go to top

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