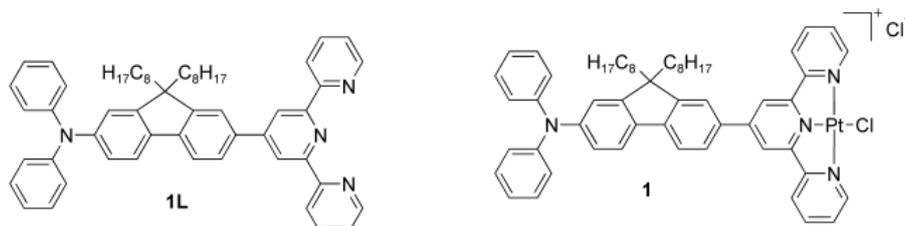


- One-Photon Photophysics and Two-Photon Absorption of 4-[9,9-Di(2-ethylhexyl)-7-diphenylaminofluoren-2-yl]-2,2':6',2''-terpyridine and Their Platinum Chloride Complexes  
Ji, Z.; Li, Y.; Pritchett, T. M.; Makarov, N. S.; Haley, J. E.; Li, Z.; Drobizhev, M.; Rebane, A.; Sun, W. *Chem.-Eur. J.* **2011**, *17*, 2479-2491.

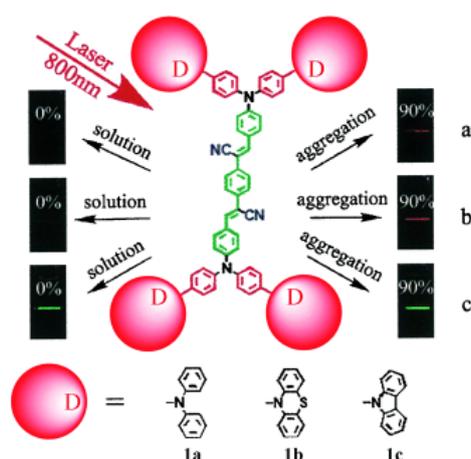
Abstract:



The synthesis, one-photon photophysics and two-photon absorption (2PA) of three dipolar D- $\pi$ -A 4-[9,9-di(2-ethylhexyl)-7-diphenylaminofluoren-2-yl]-2,2':6',2''-terpyridine and their platinum chloride complexes with different linkers between the donor and acceptor are reported. All ligands exhibit  $^1\pi,\pi^*$  transition in the UV and  $^1\pi,\pi^*/^1\text{ICT}$  (intramolecular charge transfer) transition in the visible regions, while the complexes display a lower-energy  $^1\pi,\pi^*/^1\text{CT}$  (charge transfer) transition in the visible region in addition to the high-energy  $^1\pi,\pi^*$  transitions. All ligands and the complexes are emissive at room temperature and 77 K, with the emitting excited state assigned as the mixed  $^1\pi,\pi^*$  and  $^1\text{CT}$  states at RT. Transient absorption from the ligands and the complexes were observed. 2PA was investigated for all ligands and complexes. The two-photon absorption cross-sections ( $\sigma_2$ ) of the complexes (600–2000 GM) measured by Z-scan experiment are much larger than those of their corresponding ligands measured by the two-photon induced fluorescence method. The ligand and the complex with the ethynylene linker show much stronger 2PA than those with the vinylene linker.

- Starburst Triarylamine Donor–Acceptor–Donor Quadrupolar Derivatives Based on Cyano-Substituted Diphenylaminostyrylbenzene: Tunable Aggregation-Induced Emission Colors and Large Two-Photon Absorption Cross Sections  
Su, Y.-S.; Liu, J.-W.; Jiang, Y.; Chen, C.-F. *Chem.-Eur. J.* **2011**, *17*, 2647-2655.

Abstract:

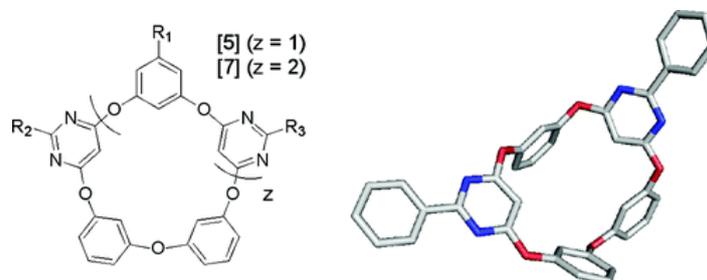


In this work, we have developed a new class of aggregation-induced emission (AIE) active compounds, in which three electron-donating diphenylamine, phenothiazine, or carbazole groups are connected to the 1, 4-positions of the benzene through bis( $\alpha$ -cyano-4-diphenylaminostyryl) conjugation bridges to form three triarylamine quadrupolar derivatives (**3 a–c**). Their one- and two-photon absorption properties have been investigated. The two-photon absorption (2PA) cross

sections measured by the open-aperture Z-scan technique were determined to be 1016, 1484, and 814 GM for **3 a–c**, respectively. From this result, the high 2PA properties of these molecules are attributed to the extended  $\pi$  system and enhanced intramolecular charge transfer from the starburst triarylamine to the cyano group. Moreover, cyano-substituted diphenylamine styrylbenzene (CNDPASB)-based compounds are very weakly fluorescent in THF, but their intensities increase by almost 230, 70, and 5 times, respectively, in water/THF (v/v 90 %) mixtures, in which they exhibit strongly enhanced red, orange, and deep yellow fluorescence emissions, respectively. This result indicates that the intramolecular vibration and rotation of these dyes is considerably restricted in nano-aggregates formed in water, leading to significant increases in fluorescence. It was found that the color tuning of the CNDPASB-based compounds could be conveniently accomplished by changing the starburst triarylamine donor moiety. Multilayer electroluminescence devices with TPBI (2,2',2''-(benzene-1,3,5-triyl)-tri(1-phenyl-1*H*-benzimidazole)) electron-transporting layers have been made, with **3 a** and **3 c** as a non-doping red–yellow emitter. The preliminary results for these multilayer devices show a maximum efficiency of 0.25 %, and electroluminescence (EL) wavelengths around 568 nm. The excellent 2PA and AIE properties of these compounds make them potential materials for biophotonic applications. reversible thermo- and pH-induced gel–sol transitions were also found. The presented work will provide a new strategy for the construction of supramolecular polymers with specific structures and properties.

- Odd-Numbered Oxacalix[n]arenes ( $n = 5, 7$ ): Synthesis and Solid-State Structures  
Van Rossom, W.; Robeyns, K.; Ovaere, M.; Van Meervelt, L.; Dehaen, W.; Maes, W. *Org. Lett.* **2011**, *13*, 126-129.

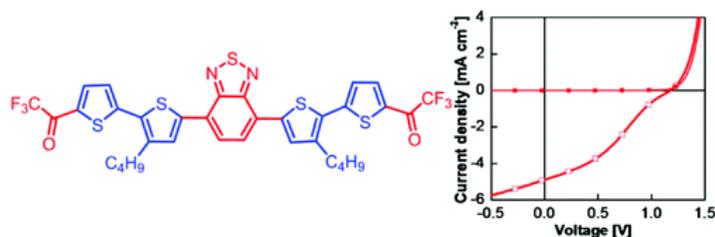
Abstract:



The critical synthetic access to odd-numbered calix[n]arenes has evidently resulted in less attention for these macrocycles, although specific molecular recognition phenomena have been observed for some of them. A straightforward fragment coupling approach has been designed, applying kinetically controlled nucleophilic aromatic substitution reaction conditions, affording odd-numbered oxacalix[n]arenes ( $n = 5, 7$ ) selectively in high yields. The solid-state conformational behavior and the oxacalix[n]arene cavity size were explored by single-crystal X-ray diffraction studies.

- A-D-A-D-A-Type Oligothiophenes for Vacuum-Deposited Organic Solar Cells  
Steinberger, S.; Mishra, A.; Reinold, E.; Müller, C. M.; Uhrich, C.; Pfeiffer, M.; Bäuerle, P. *Org. Lett.* **2011**, *13*, 90–93.

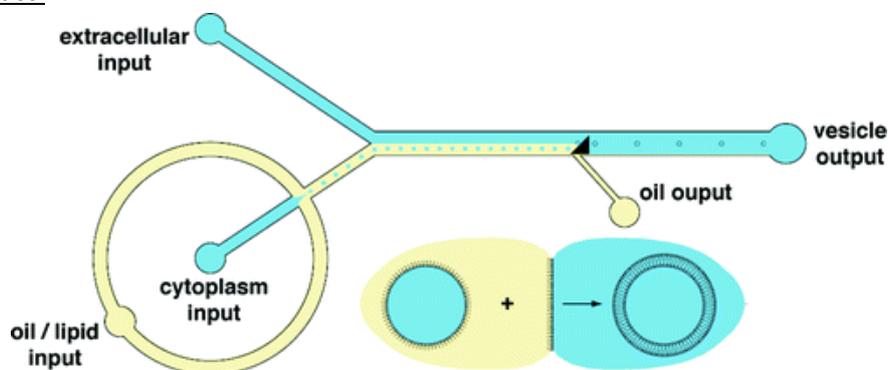
Abstract:



Novel A-D-A-D-A-type oligothiophenes incorporating electron-withdrawing benzo[*c*][1,2,5]thiadiazole (BTDA) as core and trifluoroacetyl (TFA) as terminal acceptor groups have been developed. Vacuum-processed planar heterojunction organic solar cells incorporating these new oligomers as donor and C<sub>60</sub> as acceptor showed very high open circuit voltages up to 1.17 V, resulting in power conversion efficiencies of 1.56% under AM1.5G conditions.

- Stepwise Synthesis of Giant Unilamellar Vesicles on a Microfluidic Assembly Line  
Matosevic, S.; Paegel, B. M. *J. Am. Chem. Soc.* **2011**, *133*, 2798–2800.

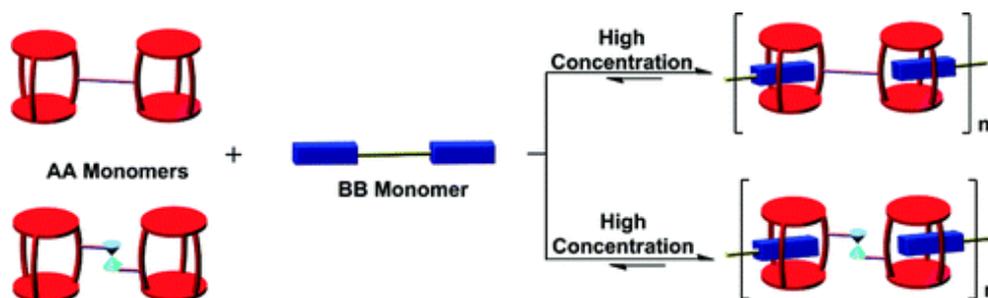
Abstract:



Among the molecular milieu of the cell, the membrane bilayer stands out as a complex and elusive synthetic target. We report a microfluidic assembly line that produces uniform cellular compartments from droplet, lipid, and oil/water interface starting materials. Droplets form in a lipid-containing oil flow and travel to a junction where the confluence of oil and extracellular aqueous media establishes a flow-patterned interface that is both stable and reproducible. A triangular post mediates phase transfer bilayer assembly by deflecting droplets from oil, through the interface, and into the extracellular aqueous phase to yield a continuous stream of unilamellar phospholipid vesicles with uniform and tunable size. The size of the droplet precursor dictates vesicle size, encapsulation of small-molecule cargo is highly efficient, and the single bilayer promotes functional insertion of a bacterial transmembrane pore.

- Supramolecular AA–BB-Type Linear Polymers with Relatively High Molecular Weights via the Self-Assembly of Bis(*m*-phenylene)-32-Crown-10 Cryptands and a Bisparaquat Derivative  
Niu, Z.; Huang, F.; Gibson, H. W. *J. Am. Chem. Soc.* **2011**, *133*, 2836–2839.

Abstract:

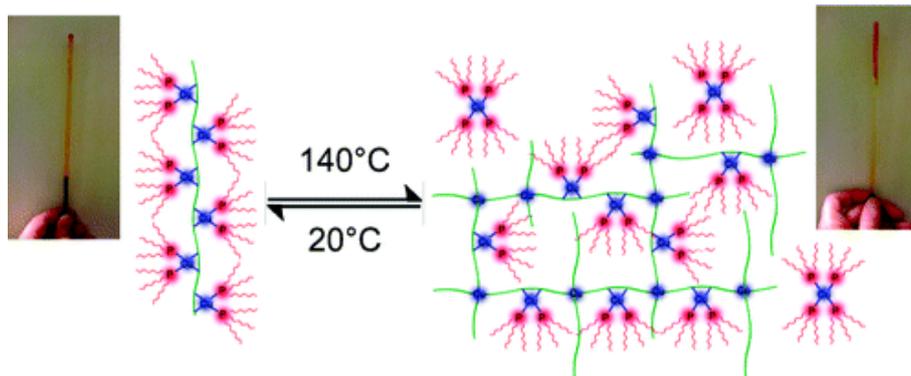


Two novel bis(*m*-phenylene)-32-crown-10-based cryptands, one bearing covalent linkages and the other metal-complex linkages, were designed and prepared. By self-assembly of these biscryptands, which can be viewed as AA monomers, and a bisparaquat, which can be viewed as a BB monomer, AA-BB-type linear supramolecular polymers with relatively high molecular weights were successfully prepared.

- A Dynamic Covalent, Luminescent Metallopolymer that Undergoes Sol-to-Gel Transition on Temperature Rise

Hatten, X.; Bell, N.; Yufa, N.; Christmann, G.; Nitschke, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 3158–3164.

Abstract:

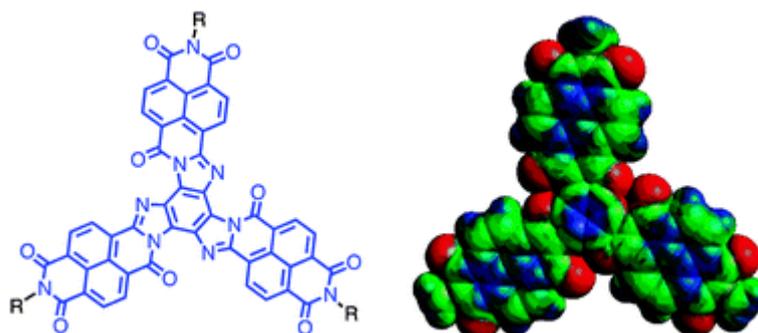


The condensation of linear diamine and dialdehyde subcomponents around copper(I) templates in the presence of bulky trioctylphosphine ancillary ligands gave a linear, conjugated polymeric material in DMSO solution. This polymer solution was observed to undergo sol-to-gel transition as the temperature was raised to 140 °C, in contrast with the behavior of most gel-forming polymers, which do so upon cooling. We attribute the sol-to-gel transition to the formation of CuIN<sub>4</sub> cross-links as the equilibria  $2[\text{CuIN}_2\text{P}_2] \rightleftharpoons [\text{CuIN}_4] + [\text{CuPn}] + (4 - n)\text{P}$  favor the right-hand side at higher temperatures. The material was also observed to exhibit thermochromism and photoluminescence, with the color and intensity of both absorption and emission exhibiting temperature dependence. This material thus responds predictably to combinations of stimuli (heat, light, mechanical shear) in an interconnected way, as is required to generate complex function.

- Novel C<sub>3</sub>-symmetric n-type tris(aryleneimidazole) and its analogs: synthesis, physical properties and self-assembly

Hanifi, D.; Cao, D.; Klivansky, L. M.; Liu, Y. *Chem. Commun.* **2011**, *47*, 3454-3456.

Abstract:

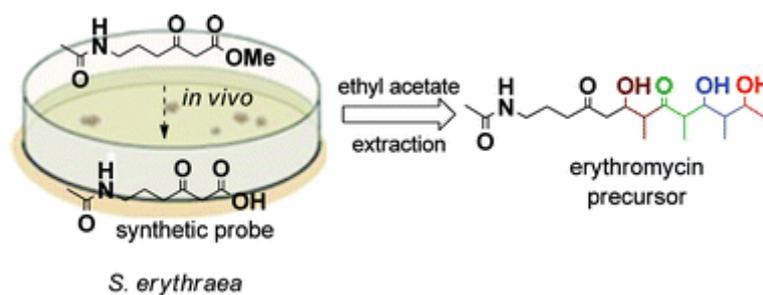


Novel n-type  $C_3$ -symmetric materials are synthesized and shown to have desirable bandgap, broad absorption and high thermal stability, thus pose as viable candidates for organic photovoltaics. The strong intermolecular interactions among the extended  $\pi$ -surfaces beget the self-assembly of nanofibers.

- In vivo trapping of polyketide intermediates from an assembly line synthase using malonyl carba(dethia)-N-acetyl cysteamines

Tosin, M.; Demydchuk, Y.; Parascandolo, J. S.; Blasco Per, C.; Leeper, F. J.; Leadlay, P. F. *Chem. Commun.* **2011**, 47, 3460-3462.

Abstract:



Early-stage intermediates in the biosynthesis of erythromycin A by *Saccharopolyspora erythraea* were intercepted by malonyl carba(dethia)-N-acetyl cysteamines, generated in vivo from the hydrolysis of the corresponding methyl esters.

- High-efficiency dye-sensitized solar cells with ferrocene-based electrolytes
- Daeneke, T.; Kwon, T.-H.; Holmes, A. B.; Duffy, N. W.; Bach, U.; Spiccia, L. *Nature Chemistry* **2011**, 3, 213-217.

Abstract:



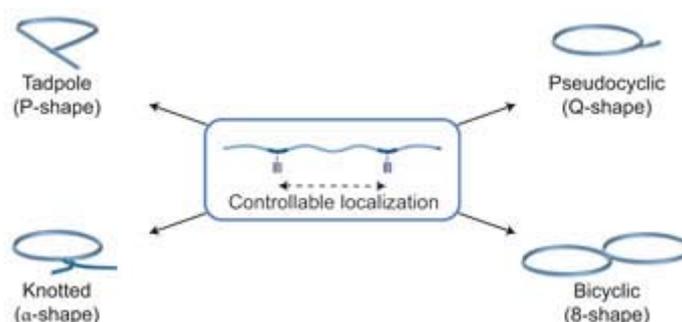
Dye-sensitized solar cells based on iodide/triiodide ( $I^-/I_3^-$ ) electrolytes are viable low-cost alternatives to conventional silicon solar cells. However, as well as providing record efficiencies of up to 12.0%, the use of  $I^-/I_3^-$  in such solar cells also brings about certain limitations that stem from its corrosive nature and complex two-electron redox chemistry. Alternative redox mediators have been investigated, but these generally fall well short of matching the performance of conventional  $I^-/I_3^-$

electrolytes. Here, we report energy conversion efficiencies of 7.5% (simulated sunlight, AM1.5,  $1,000 \text{ W m}^{-2}$ ) for dye-sensitized solar cells combining the archetypal ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) single-electron redox couple with a novel metal-free organic donor–acceptor sensitizer (Carbz-PAHTDIT). These  $\text{Fc}/\text{Fc}^+$ -based devices exceed the efficiency achieved for devices prepared using  $\text{I}^-/\text{I}_3^-$  electrolytes under comparable conditions, revealing the great potential of ferrocene-based electrolytes in future dye-sensitized solar cells applications. This improvement results from a more favourable matching of the redox potential of the ferrocene couple with that of the new donor–acceptor sensitizer.

- Controlled folding of synthetic polymer chains through the formation of positionable covalent bridges

Schmidt, B. V. K. J.; Fechler, N.; Falkenhagen, J.; Lutz, J.-F. *Nature Chemistry* **2011**, *3*, 236–240.

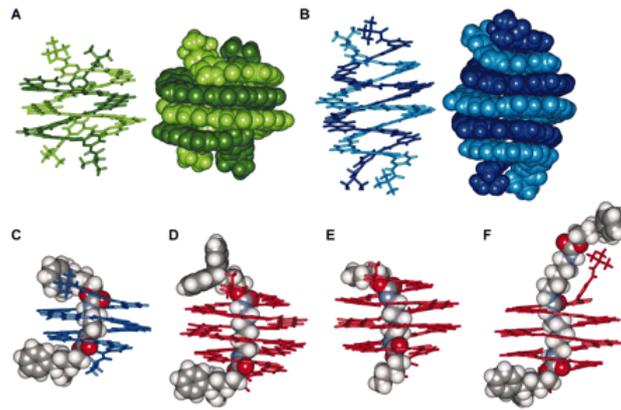
Abstract:



Covalent bridges play a crucial role in the folding process of sequence-defined biopolymers. This feature, however, has not been recreated in synthetic polymers because, apart from some simple regular arrangements (such as block co-polymers), these macromolecules generally do not exhibit a controlled primary structure—that is, it is difficult to predetermine precisely the sequence of their monomers. Herein, we introduce a versatile strategy for preparing foldable linear polymer chains. Well-defined polymers were synthesized by the atom transfer radical polymerization of styrene. The controlled addition of discrete amounts of protected maleimide at precise times during the synthesis enabled the formation of polystyrene chains that contained positionable reactive alkyne functions. Intramolecular reactions between these functions subsequently led to the formation of different types of covalently folded polymer chains. For example, tadpole (P-shaped), pseudocyclic (Q-shaped), bicyclic (8-shaped) and knotted ( $\alpha$ -shaped) macromolecular origamis were prepared in a relatively straightforward manner.

- Helix-Rod Host-Guest Complexes with Shuttling Rates Much Faster than Disassembly  
Gan, Q.; Ferrand, Y.; Bao, C.; Kauffmann, B.; Grélard, A.; Jiang, H.; Huc, I. *Science* **2011**, *331*, 1172-1175.

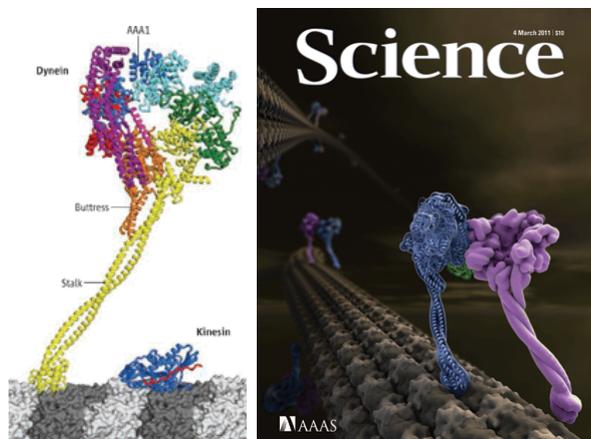
Abstract:



Dynamic assembly is a powerful fabrication method of complex, functionally diverse molecular architectures, but its use in synthetic nanomachines has been hampered by the difficulty of avoiding reversible attachments that result in the premature breaking apart of loosely held moving parts. We show that molecular motion can be controlled in dynamically assembled systems through segregation of the disassembly process and internal translation to time scales that differ by four orders of magnitude. Helical molecular tapes were designed to slowly wind around rod-like guests and then to rapidly slide along them. The winding process requires helix unfolding and refolding, as well as a strict match between helix length and anchor points on the rods. This modular design and dynamic assembly open up promising capabilities in molecular machinery.

- Molecular Motors, Beauty in Complexity  
Spudich, J. A. *Science* **2011**, *331*, 1143-1144.

Abstract:



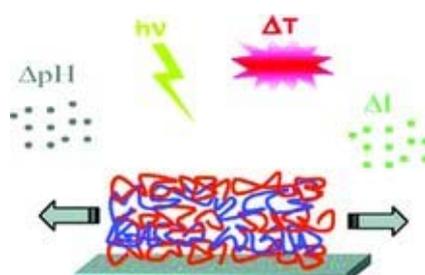
Among the most fascinating enzymes are the molecular motors, which exquisitely couple adenosine triphosphate (ATP) hydrolysis to directional mechanical motion. They power the movement of intracellular vesicles, chromosomes, and messenger RNA–protein complexes through the cytoplasm of nearly all eukaryotic cells, using actin filaments and microtubules as their tracks. A prominent theme in these motors is allostery, or communications that occur across the enzyme at several nanometer distances. Chemical events occurring in the motor's active site, for instance, are coordinated with tight binding of the motor to the track along which it moves, and then its subsequent release, and with mechanical elements that amplify small movements occurring near the active site. In the 1980s, researchers used quantitative *in vitro* motility assays, sensitive to single molecules, to study two of the three major classes of motor enzymes: the microtubule-based kinesin family and the actin-based myosin family. In the 1990s, investigators solved the crystal structures of

kinesin 1 (1) and muscle myosin II (2). These complementary approaches ushered in a new era of understanding the mechanisms of these molecular machines. Dynein, the third important class of molecular motor, is a complex that processively moves along microtubules in the opposite direction to kinesin 1. Although single molecule assays have been applied to dynein, detailed structural information on this mammoth machine has remained elusive, until now. On page 1159 of this issue, Carter *et al.* (3) report a crystal structure for a 610-kD homodimer of yeast cytoplasmic dynein. The structure reveals surprises about how this massive molecular motor might work.

- Dynamic Aspects of Films Prepared by a Sequential Deposition of Species: Perspectives for Smart and Responsive Materials

Lavalle, P.; Voegel, J.-C.; Vautier, D.; Senger, B.; Schaaf, P.; Ball, V. *Adv. Mater.* **2011**, *23*, 1191-1221.

Abstract:

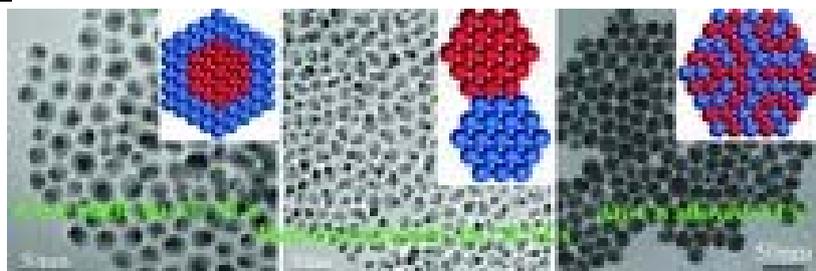


The deposition of surface coatings using a step-by-step approach from mutually interacting species allows the fabrication of so called “multilayered films”. These coatings are very versatile and easy to produce in environmentally friendly conditions, mostly from aqueous solution. They find more and more applications in many hot topic areas, such as in biomaterials and nanoelectronics but also in stimuli-responsive films. We aim to review the most recent developments in such stimuli-responsive coatings based on layer-by-layer (LBL) depositions in relationship to the properties of these coatings. The most investigated stimuli are based on changes in ionic strength, temperature, exposure to light, and mechanical forces. The possibility to induce a transition from linear to exponential growth in thickness and to change the charge compensation from “intrinsic” to “extrinsic” by controlling parameters such as temperature, pH, and ionic strength are the ways to confer their responsiveness to the films. Chemical post-modifications also allow to significantly modify the film properties.

- Bimetallic Nanocrystals: Liquid-Phase Synthesis and Catalytic Applications

Wang, D.; Li, Y. *Adv. Mater.* **2011**, *23*, 1044-1060.

Abstract:



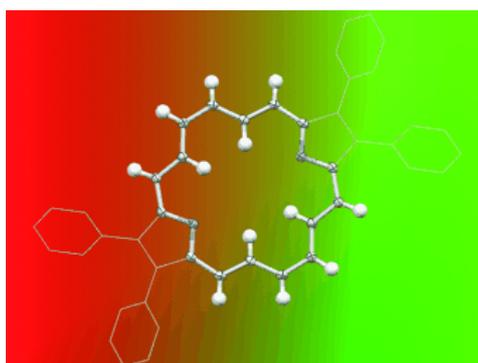
Bimetallic nanocrystals (NCs) with core/shell, heterostructure, or intermetallic and alloyed structures are emerging as more important materials than monometallic NCs. They are expected to display not only a combination of the properties associated with two distinct metals, but also new properties and capabilities due to a synergy between the two metals. More importantly, bimetallic NCs usually

show composition-dependent surface structure and atomic segregation behavior, and therefore more interesting applied potentials in various fields including electronics, engineering, and catalysis. Compared with monometallic NCs, preparation of bimetallic NCs is much more complicated and difficult to be achieved. In recent years, researchers from many groups have made great efforts in this area. This review highlights the recent progress in the chemical synthesis of bimetallic NCs. The control over morphology, size, composition, and structure of bimetallic NCs as well as the exploration of their properties and applications are discussed.

- How Should Aromaticity Be Described in Porphyrinoids?

Bröring, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 2436-2438.

Abstract:

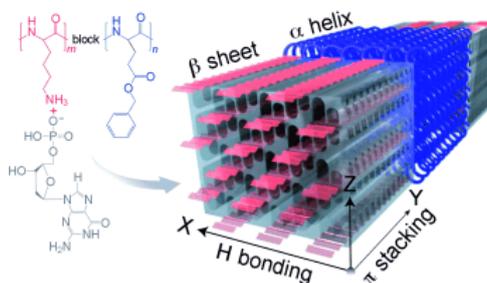


“Porphyrins really are the [18]annulenes of nature”—This is the title of a report dealing with a new macrocycle (see structure; gray C, white H, blue N), which can be considered as either a porphyrin or an [18]annulene. The spectroscopic data prove the aromatic and porphyrinoid character of the new compound, and support the simple concept of a  $(4n+2)\pi$  main conjugation pathway as a key criterion for porphyrinoid Hückel aromaticity.

- Self-Assembled Polymeric Supramolecular Frameworks

Houbenov, N.; Haataja, J. S.; Iatrou, H.; Hadjichristidis, N.; Ruokolainen, J.; Faul, C. F. J.; Ikkala, O. *Angew. Chem. Int. Ed.* **2011**, *50*, 2516-2520.

Abstract:



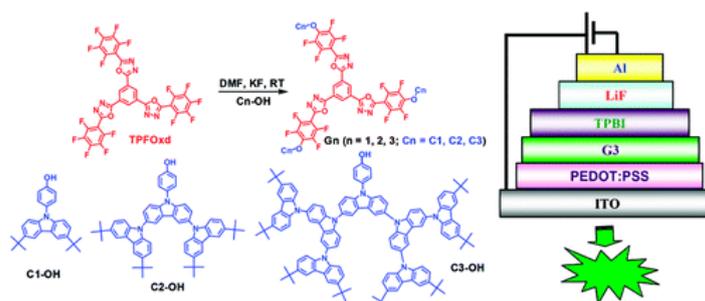
Within the framework: Ionic complexation of diblock copolypeptide poly( $\gamma$ -benzyl-L-glutamate)-block-poly(L-lysine) (PBLG-b-PLL) with 2'-deoxyguanosine 5'-monophosphate (dGMP, gray) generates a polymeric supramolecular framework solid with self-assembled cages based on two orthogonal shape-persistent motifs: PBLG  $\alpha$  helices (blue) and PLL  $\beta$  sheets (red), which in turn are held together by shape-persistent hydrogen-bonded G-ribbons.

- Synthesis and Properties of Dendritic Emitters with a Fluorinated Starburst Oxadiazole Core and Twisted Carbazole Dendrons

Zhao, Z.-H.; Jin, H.; Zhang, Y.-X.; Shen, Z. *Macromolecules* **2011**, *44*, 1405–1413.

Abstract:

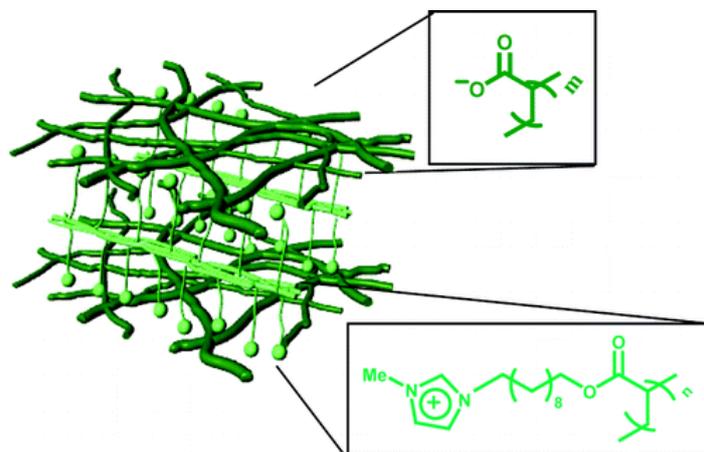
10



Three generations of novel dendrimers (G1, G2, and G3) with an electron-deficient fluorinated starburst oxadiazole core and twisted carbazoles as dendrons were synthesized via aromatic nucleophilic substitution reaction at ambient temperature by the weak base potassium fluoride with a high selectivity in a nearly quantitative yield, which was attributed to the high reactivity of the *para* fluorine atom activated by oxadiazole and multiple fluorine atoms.  $^1\text{H}$  NMR,  $^{19}\text{F}$  NMR, elemental analysis, and MALDI-TOF MS results confirmed the designed chemical structures. Varying the generation to gradually modify the dendrons could gradually modulate the HOMO–LUMO energy band gaps of  $G_n$ , which was verified by cyclic voltammetry results. Photoluminescent spectra showed the dual fluorescence emission of the dendrimers in solutions, which indicated that twist intramolecular charge transfer occurred between oxadiazole and carbazole separated by nonconjugated bonds. The  $G_n$ -based devices with the configuration of ITO/PEDOT:PSS/ $G_n$ /TPBI/AIQ/LiF/Al displayed a stable green emission in their electroluminescent spectra with a gradual increase in external quantum efficiency and current efficiency for higher-generation dendrimers, owing to gradually improved charge transport. The device with G3 possessed the lowest turn-on voltage along with the highest external quantum efficiency of 1.49%, maximum current efficiency of 4.6 cd/A, and a high luminance of 4882 cd/m<sup>2</sup>, indicating that it had the best carrier balance.

- Formation of a Liquid-Crystalline Interpenetrating Poly(ionic liquid) Network Hydrogel  
Becht, G. A.; Sofos, M.; Seifert, S.; Firestone, M. A. *Macromolecules* **2011**, *44*, 1421–1428.

Abstract:



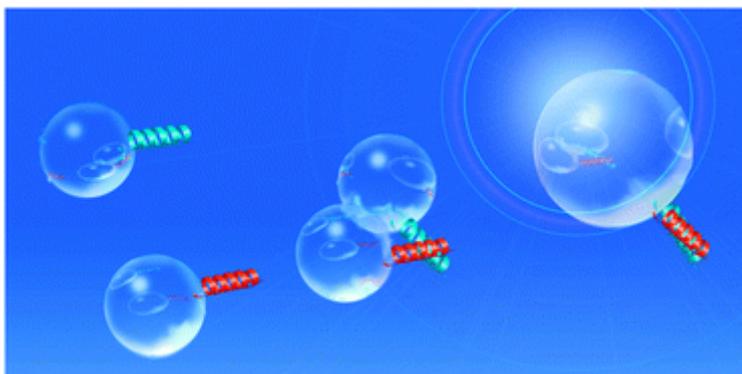
Preparation of a liquid-crystalline ionic-liquid (IL)-based interpenetrating polymer network (IPN) is described. The IPN is prepared sequentially by first photopolymerizing a self-assembled aqueous mixture of an IL monomer (1-(10-(acryloyloxy)decyl)-3-methylimidazolium chloride) that possesses

an acryloyl moiety at the terminus of a C<sub>10</sub> alkyl chain of the IL cation. In the second step, an acrylate counteranion is introduced and then photopolymerized to yield a durable self-supporting network polymer. Thermal analysis indicates the formation of a homogeneous (well-blended constituent polymers) IPN. The IPN adopts a lamellar structure possessing some residual in-plane tetragonal perforations, as evidenced by small-angle X-ray scattering (SAXS). The IPN can absorb large quantities of water, swelling to nearly 60 times its original volume, but retains mechanical integrity making it a durable hydrogel.

- Model systems for membrane fusion

Robson Marsden, H.; Tomatsu, I.; Kros, A. *Chem. Soc. Rev.* **2011**, *40*, 1572-1585.

Abstract:

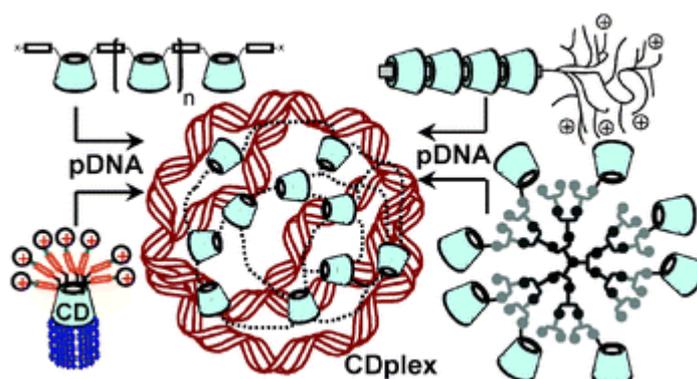


Membrane fusion has an overarching influence on living organisms. The fusion of sperm and egg membranes initiates the life of a sexually reproducing organism. Intracellular membrane fusion facilitates molecular trafficking within every cell of the organism during its entire lifetime, and virus-cell membrane fusion may signal the end of the organism's life. Considering its importance, surprisingly little is known about the molecular-level mechanism of membrane fusion. Due to the complexity of a living cell, observations often leave room for ambiguity in interpretation. Therefore artificial model systems composed of only a few components are being used to further our understanding of controlled fusion processes. In this *critical review* we first give an overview of the hypothesized mechanism of membrane fusion and the techniques that are used to investigate it, and then present a selection of non-targeted and targeted model systems, finishing with current applications and predictions on future developments (85 references).

- Cyclodextrin-based gene delivery systems

Ortiz Mellet, C.; García Fernández, J. M.; Benito, J. M. *Chem. Soc. Rev.* **2011**, *40*, 1586-1608.

Abstract:



Cyclodextrin (CD) history has been largely dominated by their unique ability to form inclusion complexes with guests fitting in their hydrophobic cavity. Chemical functionalization was soon recognized as a powerful mean for improving CD applications in a wide range of fields, including drug delivery, sensing or enzyme mimicking. However, 100 years after their discovery, CDs are still perceived as novel nanoobjects of undeveloped potential. This *critical review* provides an overview of different strategies to promote interactions between CD conjugates and genetic material by fully exploiting the inside-outside/upper-lower face anisotropy of the CD nanometric platform. Covalent modification, self-assembling and supramolecular ligation can be put forward with the ultimate goal to build artificial viruses for programmed and efficient gene therapy (222 references).