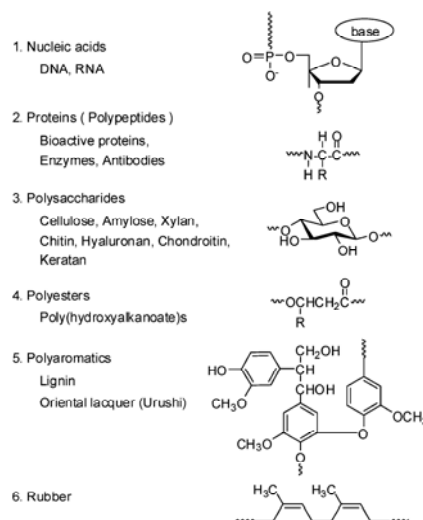


- Enzymatic Polymer Synthesis: An Opportunity for Green Polymer Chemistry
Kobayashi, S.; Makino, A. *Chem. Rev.* **2009**, *109*, 5288–5353.

Abstract:

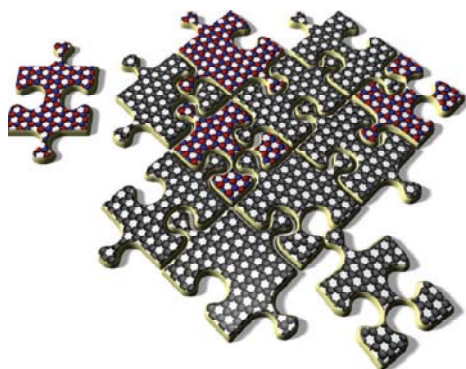
Typical Examples of Natural Biomacromolecules



Polymeric materials, natural and unnatural, are indispensable to the modern society. They are widely used from everyday life usages as commodity materials to industry and technology usages in the fields such as electronics, machinery, communications, transportations, pharmacy, and medicine as highly advanced materials. Today, it is hard to think of the present society without polymeric materials.

- Hybridized Graphene Nanoscale Patchworks
Rubio, A. *Nature Materials* **2010**, *9*, 379-380.

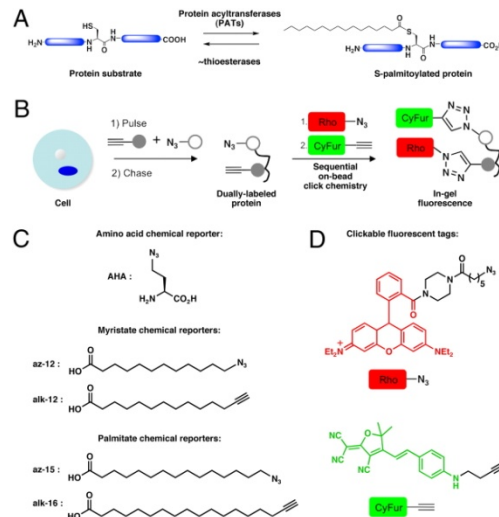
Abstract:



Patching carbon and boron nitride nanodomains emerges as an efficient way to engineer bandgaps in graphene, opening a new avenue for optoelectronic devices. Carbon is arguably the element that best represents the emergence of new phenomena and properties when dimensionality or size are reduced. Fullerenes¹, nanotubes², nanoribbons and graphene³ can be considered as the pieces available in the carbon-only 'Lego' of nanoscience, all of which show excellent electronic, mechanical and thermal properties.

- Tandem fluorescence imaging of dynamic S-acylation and protein turnover
Zhang, M. M.; Tsou, L. K.; Charron, G.; Raghavan, A. S.; Hang, H. C. *Proc. Nat. Acad. Sci.* **2010**, *107*, 8627-8632.

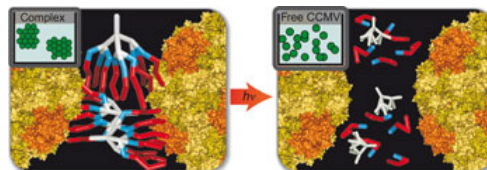
Abstract:



The functional significance and regulation of reversible S-acylation on diverse proteins remain unclear because of limited methods for efficient quantitative analysis of palmitate turnover. Here, we describe a tandem labeling and detection method to simultaneously monitor dynamic S-palmitoylation and protein turnover. By combining S-acylation and cotranslational fatty acid chemical reporters with orthogonal clickable fluorophores, dual pulse-chase analysis of Lck revealed accelerated palmitate cycling upon T-cell activation. Subsequent pharmacological perturbation of Lck palmitate turnover suggests yet uncharacterized serine hydrolases contribute to dynamic S-acylation in cells. In addition to dually fatty-acylated proteins, this tandem fluorescence imaging method can be generalized to other S-acylated proteins using azidohomoalanine as a methionine surrogate. The sensitivity and efficiency of this approach should facilitate the functional characterization of cellular factors and drugs that modulate protein S-acylation. Furthermore, diverse protein modifications could be analyzed with this tandem imaging method using other chemical reporters to investigate dynamic regulation of protein function.

- Self-assembly and optically triggered disassembly of hierarchical dendron–virus complexes
Kostiainen, M. A.; Kasyutich, O.; Cornelissen, J. J. L. M.; Nolte, R. J. M. *Nature Chemistry* **2010**, 2, 394 – 399.

Abstract:

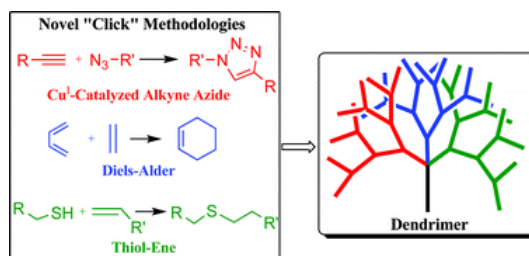


Nature offers a vast array of biological building blocks that can be combined with synthetic materials to generate a variety of hierarchical architectures. Viruses are particularly interesting in this respect because of their structure and the possibility of them functioning as scaffolds for the preparation of new biohybrid materials. We report here that cowpea chlorotic mottle virus particles can be assembled into well-defined micrometre-sized objects and then reconverted into individual viruses by application of a short optical stimulus. Assembly is achieved using photosensitive dendrons that bind on the virus surface through multivalent interactions and then act as a molecular glue between the virus particles. Optical triggering induces the controlled decomposition and charge switching of dendrons, which results in the loss of multivalent interactions and the release of virus particles. We

demonstrate that the method is not limited to the virus particles alone, but can also be applied to other functional protein cages such as magnetoferritin.

- « Click » methodologies: efficient, simple and greener routes to design dendrimers
Franc, G.; Kakkar, A. K. *Chem. Soc. Rev.* **2010**, *39*, 1536 – 1544.

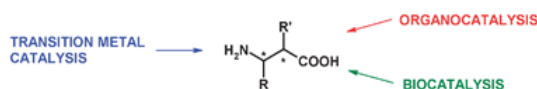
Abstract:



Designing dendrimers that are monodisperse hyperbranched macromolecules and offer significant potential in numerous scientific fields, is becoming a major topical area in modern research. Among the challenges of the 21st century, synthetic methodologies that increase efficiency of conversion and a greener chemistry approach, are expected to lead the way in the quest to build novel nanomaterials. The recent entry of so-called « click » reactions that include Diels–Alder, Cu^I-catalyzed Huisgen cycloaddition and thiol-ene coupling, have generated real stimulus not only in developing elegant materials of choice, but also in making the leap to industrial scale build-up of dendritic macromolecules. This *tutorial review* takes on the task of demonstrating the simplicity of these « click » reactions and the advantages they offer from a synthetic view point in developing mono- to multifunctional dendrimers. A brief introduction to « click » chemistry is followed by a chronological survey of developments in the field, and the impact these have had in designing novel dendritic macromolecules. The review is intended to introduce scientists to these highly efficient methodologies with demonstrated potential, and provide impetus for further growth of the area.

- Recent advances in the catalytic asymmetric synthesis of β-amino acids
Weiner, B.; Szymański, W.; Janssen, D. B.; Minnaard, A. J.; Feringa, B. L. *Chem. Soc. Rev.* **2010**, *39*, 1656 – 1691.

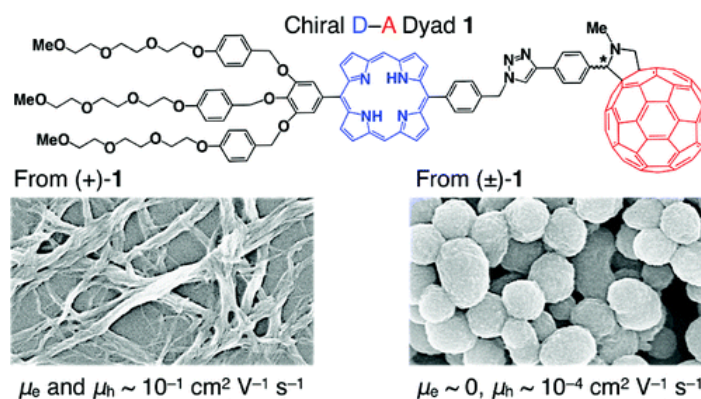
Abstract:



In this *critical review*, the progress in catalytic asymmetric synthesis of β-amino acids is discussed, covering the literature since 2002. The review treats transition metal catalysis, organocatalysis and biocatalysis and covers the most important synthetic methods, such as hydrogenation, the Mannich reaction and conjugate additions (160 references).

- Chiroselective Assembly of a Chiral Porphyrin–Fullerene Dyad: Photoconductive Nanofiber with a Top-Class Ambipolar Charge-Carrier Mobility
Hizume, Y.; Tashiro, K.; Charvet, R.; Yohei, Y.; Saeki, A.; Seki, S.; Aida, T. *J. Am. Chem. Soc.* **2010**, *132*, 6628–6629.

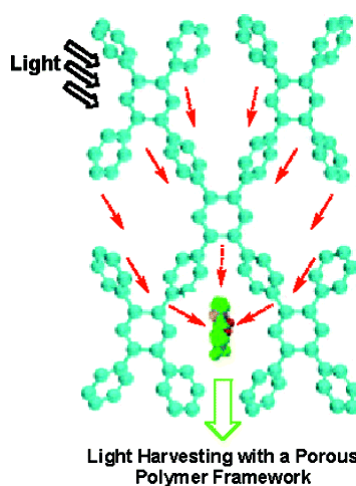
Abstract:



Upon slow admission of MeOH, the enantiomerically pure form of chiral amphiphilic porphyrin–fullerene dyad 1 in CH_2Cl_2 self-assembles at 25 °C into nanofibers with a built-in donor/acceptor heterojunction, while its racemic form, under identical conditions, self-assembles into submicrometer-sized spheres with a donor/acceptor arrangement essentially different from that in the nanofiber assembly. Although a cast film of the latter hardly shows a photoconducting profile on micrometer-gap electrodes, the former sample clearly displays photoconduction with an ambipolar charge-transporting character. The electron and hole mobilities under zero electric field, as estimated from time-of-flight profiles, are 0.14 and 0.10 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, which are comparable to or even better than those reported for top-class organic materials with a donor/acceptor heterojunction.

- Light-Harvesting Conjugated Microporous Polymers: Rapid and Highly Efficient Flow of Light Energy with a Porous Polyphenylene Framework as Antenna
Chen, L.; Honsho, Y.; Seki, S.; Jiang, D. *J. Am. Chem. Soc.*, **2010**, *132*, 6742–6748.

Abstract:



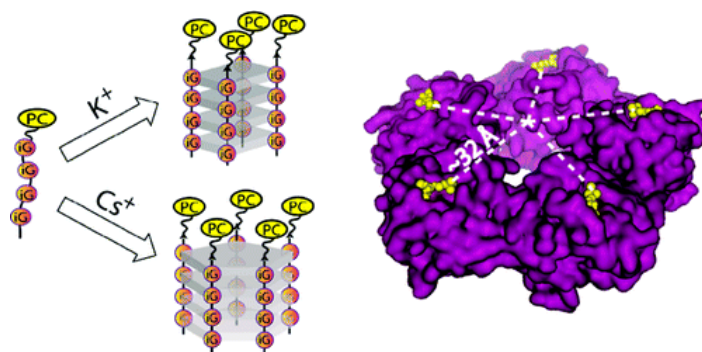
The molecular design of light-harvesting antennae requires not only the segregation of a large number of chromophore units in a confined nanospace but also the cooperation of these units in achieving highly efficient energy transduction. This article describes the synthesis and functions of a polyphenylene-based conjugated microporous polymer (PP-CMP). PP-CMP was recently designed and synthesized by Suzuki polycondensation reaction and used as an antenna for the noncovalent construction of a light-harvesting system. In contrast to linear polyphenylene, PP-CMP consists of conjugated three-dimensional polyphenylene scaffolds and holds inherent porous structure with uniform pore size (1.56 nm) and large surface area (1083 $\text{m}^2 \text{ g}^{-1}$). It emits blue photoluminescence, is capable of excitation energy migration over the framework, and enables rapid transportation of

charge carrier with intrinsic mobility as high as $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The microporous structure of PP-CMP allows for the spatial confinement of energy-accepting coumarin 6 molecules in the pores and makes the high-throughput synthesis of light-harvesting systems with designable donor–acceptor compositions possible. Excitation of the PP-CMP skeleton leads to brilliant green emission from coumarin 6, with an intensity 21-fold as high as that upon direct excitation of coumarin 6 itself, while the fluorescence from PP-CMP itself is wholly quenched as a result of energy transfer from the light-harvesting PP-CMP framework to coumarin 6. The PP-CMP skeleton is highly cooperative, with an average of 176 phenylene units working together to channel the excitation energy to one coumarin 6 molecule, and features the energy-transfer process with quick, efficient, and vectorial character. These unique characteristics clearly originate from the conjugated porous structure and demonstrate the usefulness of CMPs in the exploration of π -electronic functions, in addition to their gas adsorption properties thus far reported.

- Altered Binding of a Multimeric Protein by Changing the Self-Assembling Properties of its Substrate

Rosenzweig, B. A.; Ross, N. T.; Adler, M. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **2010**, *132*, 6749–6754.

Abstract:

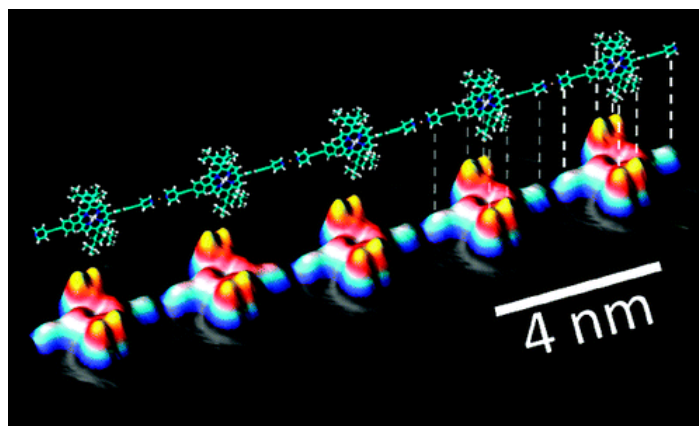


Artificially controlled cell recognition has potentially far-reaching applications in both the understanding and altering of biological function. The event of recognition often involves a multimeric protein binding a cellular membrane. While such an interaction is energetically favorable, it has been surprisingly underexploited in artificial control of recognition. Herein we describe how changing properties of substrate (phosphocholine, PC) self-assembly can affect both binding behavior and substrate affinity to a pentameric recognition protein (C-reactive protein, CRP). PC was modified with a short, self-assembling DNA strand to make the substrate self-assembly sensitive and responsive to ionic environment. A significant shift in CRP binding affinity was observed when substrates were assembled in the presence of Cs^+ rather than K^+ . Furthermore, alteration of the linker length tethering PC to DNA showed trends similar to other multivalent systems. In optimizing these linker lengths, positive cooperativity increased and K_d of the substrate assembly to CRP improved roughly 1000-fold. Such experiments both inform our understanding of biological, multivalent interactions in self-assembling systems and present a potential method to exogenously control events in cell recognition.

- Self-Assembly of Flexible One-Dimensional Coordination Polymers on Metal Surfaces
Heim, D.; Ecija, D.; Seufert, K.; Auwärter, W.; Aurisicchio, C.; Fabbro, C.; Bonifazi, D.; Barth, J. *V. J. Am. Chem. Soc.* **2010**, *132*, 6783–6790.

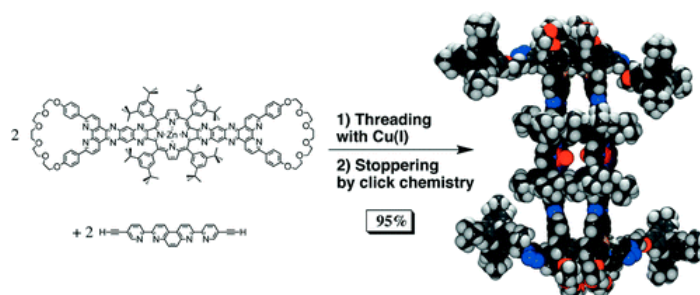
Abstract:

6



We employed a *de novo* synthesized porphyrin module to construct one-dimensional (1D) Cu-coordinated polymers on Cu(111) and Ag(111) surfaces. The programmed geometry and functionality of the molecular module together with its conformational flexibility and substrate interaction yields sinuous metal–organic polymeric assemblies, based on an unusual two-fold Cu–pyridyl coordination motif. An analysis of scanning tunneling microscopy (STM) data reveals the occurrence of two enantiomers, resulting from the surface confinement that deconvolutes the module in 2D-chiral conformational isomers. The stereoisomers exhibit site-specific surface anchoring, from whence three discrete orientations are possible for each species. Their sequence and mutual arrangement determine direction and curvature of the metal–organic chains. The Cu-coordinated polymers are very similar on both Cu(111) and Ag(111), where their formation is induced by intrinsic and coevaporated adatoms, respectively, which indicates that the lateral bonding motif is predominantly independent of the substrate. In addition, molecular manipulation experiments show the collective motion of entire segments of the Cu-coordinated multi-porphyrin polymers.

- Templated Synthesis of Cyclic [4]Rotaxanes Consisting of Two Stiff Rods Threaded through Two Bis-macrocycles with a Large and Rigid Central Plate as Spacer
Collin, J.-P.; Durola, F.; Frey, J. ; Heitz, V. ; Reviriego, F.; Sauvage, J.-P.; Trolez, Y.; Rissanen, K. *J. Am. Chem. Soc.* **2010**, *132*, 6840–6850.

Abstract:

Two related cyclic [4]rotaxanes consisting of double macrocycles and rigid rods incorporating two bidentate chelates have each been prepared in high yield. The first step is a multigathering and threading reaction driven by coordination of two different bidentate chelates (part of either the rings or the rods) to each copper(I) center so as to afford the desired precursor. In both cases, the assembly step is done under very mild conditions, and it is quantitative. The second key reaction is the stopper-attaching reaction, based on click chemistry. Even if the quadruple stoppering reaction is not quantitative, it is relatively high-yielding (60% and 95%), and the copper-driven assembly process

is carried out at room temperature without any aggressive reagent. The final copper-complexed [4]rotaxanes obtained contain two aromatic plates roughly parallel to one another located at the center of each bis-macrocycle. In the most promising case in terms of host-guest properties, the plates are zinc(II) porphyrins of the tetra-aryl series. The compounds have been fully characterized by various spectroscopic techniques (^1H NMR, mass spectrometry, and electronic absorption spectroscopy). Unexpectedly, the copper-complexed porphyrinic [4]rotaxane could be crystallized as its 4PF_6^- salt to afford X-ray quality crystals. The structure obtained is in perfect agreement with the postulated chemical structure of the compound. It is particularly attractive in terms of symmetry and molecular aesthetics. The distance between the zinc atoms of the two porphyrins is 8.673 \AA , which is sufficient to allow insertion between the two porphyrinic plates of small ditopic basic substrates able to interact with the central porphyrinic Zn atoms. This prediction has been confirmed by absorption spectroscopy measurements in the presence of various organic substrates. However, large substrates cannot be introduced in the corresponding recognition site and are thus complexed mostly in an exo fashion, being located outside the receptor cavity. Noteworthy, the stability constants of the 1:1 host-guest complexes are high (10^7 M^{-1}).

- Dipyrenylcalix[4]arene: A Fluorescence-Based Chemosensor for Trinitroaromatic Explosives
Lee, Y. H.; Liu, H.; Lee, J. Y.; Kim, S. H.; Kim, S. K.; Sessler, J. L.; Kim, Y.; Kim, J. S. *Chem. Eur. J.* **2010**, *16*, 5895-5901.

Abstract:

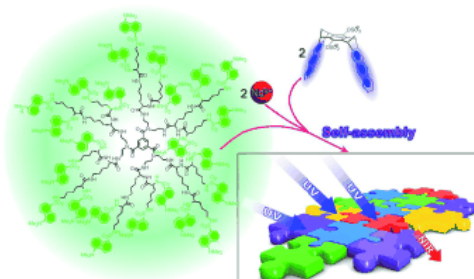


A new chemosensor-based approach to the detection of nitroaromatics is described. It involves the analyte-induced quenching of excimer emission of a dipyrenyl calix[4]arene (**L**). The chemical and photophysical properties of the complexes formed between **L** and mono-, di-, and trinitrobenzene, and di- and trinitrotoluene were studied in acetonitrile and chloroform by using ^1H NMR, UV/Vis, and fluorescence spectroscopy. Fluorescence spectroscopy revealed that the trinitroaromatics engendered the largest response among the various substrates tested, with the sensitivity for these analytes being correspondingly high. Quantitative analysis of the fluorescence titration profile generated from the titration of **L** with TNT provided evidence that this particular functionalized calix[4]arene receptor allows for the detection of TNT down to the low ppb level in CH_3CN . A single-

crystal X-ray diffraction analysis revealed that in the solid state the complex **L**-TNT consists of a supramolecular crystalline polymeric structure, the formation of which appears to be driven by intermolecular π - π interactions between two pyrene units and a TNT molecule held at a distance of 3.2-3.6 Å, as well as by intra- and intermolecular hydrogen-bonds among the amide linkages. Nevertheless, the changes in the ^1H NMR, UV/Vis, and fluorescence spectrum, including sharp color changes, are ascribed to a charge-transfer interaction arising from complementary π - π overlap between the pyrene subunits and the bound trinitroaromatic substrates. A number of ab initio calculations were also carried out and, considered in concert, they provide further support for the proposed charge-transfer interactions, particularly in the case of **L**-TNT.

- A Light-Harvesting Antenna Resulting from the Self-Assembly of Five Luminescent Components: A Dendrimer, Two Clips, and Two Lanthanide Ions
Ming Tong, G. S.; Law, Y.-C.; Kui, S. C. F.; Zhu, N.; Leung, K. H.; Phillips, D. L.; Che, C.-M. *Chem. Eur. J.* **2010**, *16*, 6048-6055.

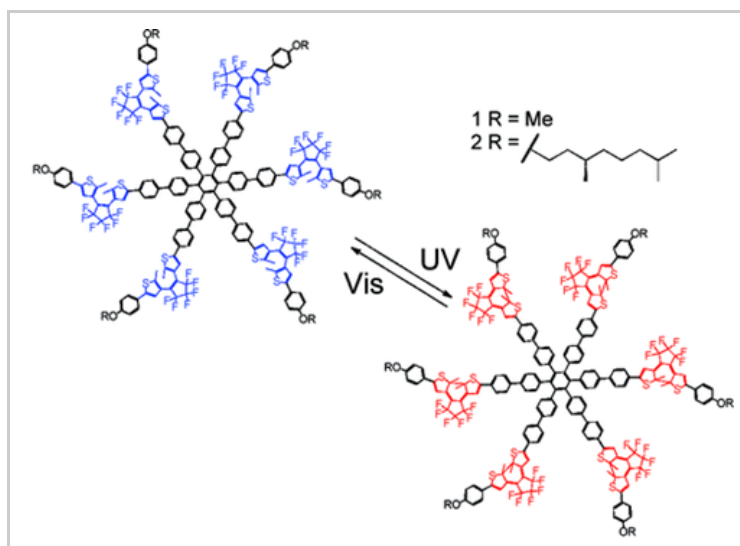
Abstract:



We have investigated the self-assembly of three luminescent species in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$, namely: 1) a polylysine dendrimer (**D**) composed of 21 aliphatic amide units and 24 green luminescent dansyl chromophores at the periphery, 2) a molecular clip (**C**) with two blue luminescent anthracene sidewalls and a benzene bridging unit that bears two sulfate groups in the *para* position, and 3) a near infrared (NIR)-emitting Nd^{3+} ion. For purposes of comparison, analogous systems have also been investigated in which Gd^{3+} replaced Nd^{3+} . The dendrimer and the clip can bind Nd^{3+} ions with formation of $[\text{D}-2 \text{Nd}^{3+}]$ and $[\text{C}-\text{Nd}^{3+}]$ complexes, in which energy transfer from dansyl and, respectively, anthracene to Nd^{3+} ion takes place with 65 and 8 % efficiency, in air-equilibrated solution. In the case of $[\text{C}-\text{Nd}^{3+}]$, the energy-transfer efficiency is quenched by dioxygen, thereby showing that the energy donor is the lowest triplet excited state of anthracene. In $[\text{D}-2 \text{Nd}^{3+}]$ the intrinsic emission efficiency of Nd^{3+} is much higher (*ca.* 5 times) than in $[\text{C}-\text{Nd}^{3+}]$ because of a better protection of the excited lanthanide ion towards nonradiative deactivation caused by interaction with solvent molecules. By mixing solutions of **D**, Nd^{3+} , and **C** with proper concentrations, a supramolecular structure with five components of three different species, $[\text{D}-2 \text{Nd}^{3+}-2 \text{C}]$, is formed. The excitation light absorbed by the clips is transferred with 100 % efficiency to the dansyl units of the dendrimer and then to the Nd^{3+} ions with 65 % efficiency either in the presence or absence of dioxygen. These results show that the $[\text{D}-2 \text{Nd}^{3+}-2 \text{C}]$ complex is able to efficiently harvest UV light by the 24 dansyl units of the dendrimer and the four anthracene chromophores of the two clips, and efficiently transfer it to the encapsulated Nd^{3+} ions that emit in the NIR spectral region.

- Symmetric Six-Fold Arrays of Photo- and Electrochromic Dithienylethene Switches
Areephong, J.; Logtenberg, H.; Browne, W. R.; Feringa, B. L. *Org. Lett.* **2010**, *12*, 2132–2135.

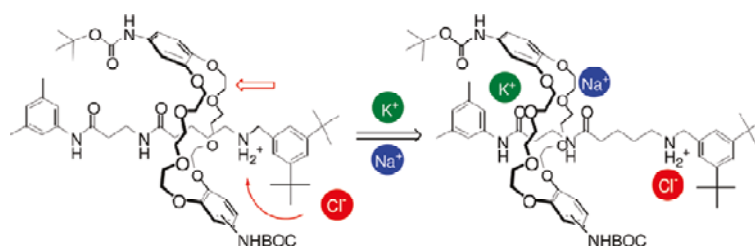
Abstract:



The direct synthesis of six-fold symmetric hexaphenylbenzenes with multiple photochromic dithienylethene units via a cobalt-catalyzed cyclotrimerization is reported. This approach allows for six photochromic units to be held in proximity with a well-defined spatial separation without affecting the photochromic properties of each unit. The design and synthesis of highly symmetric (e.g., star-shaped) macromolecules such as hexaarylbenzenes are of current interest in material science owing to their potential for application in host-guest systems, self-assembly, energy storage in chromophore aggregates, and liquid crystal technologies, through the control they provide over the orientation of functional units. Hexaarylbenzenes, due to their symmetry and relative rigidity, are key structural components on which to assemble, in a highly spatially controlled manner, redox and photoresponsive molecular units. Assemblies containing multiple redox- and photoactive units require, in addition to a rigid scaffold, robust and synthetically accessible functional units.

- Synthesis and Investigation of Host-[2]Rotaxanes That Bind Metal Cations
Wang, X.; Zhu, J.; Smithrud, D. B. *J. Org. Chem.* **2010**, *75*, 3358–3370.

Abstract:



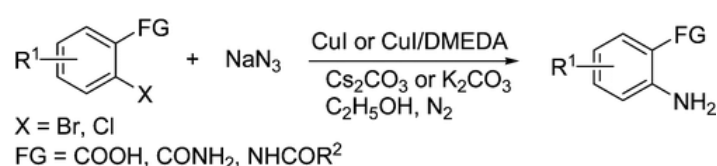
Materials that bind metal cations are highly sought after for new devices. In this report, we show that rotaxanes can transfer metal cations with picrate, perchlorate, or chloride counterions from an aqueous solution into chloroform. The rotaxanes contain a dibenzyl-24-crown-8 ether as the wheel with either a benzyl-18-crown-6 ether (CEBG-R1–3) or a 3,5-dimethylbenzyl moiety (ArBG-R) as one blocking group. Alkali and alkaline picrate salts were efficiently extracted from an aqueous solution, presented in the millimolar range, into chloroform. Large association constants were derived for the complexes in chloroform, especially for the divalent cation Mg^{2+} . Switching the counterion to chloride greatly diminished the amount of salt extracted. To explore the transfer mechanism of the rotaxanes, a comparison was made in the amount of $NaClO_4$, $KClO_4$, $NaCl$, and KCl extracted by CEBG-R1, ArBG-R, benzyl-18-crown-6 ether (B18C6), and two model compounds, which were used to represent the crown-ether blocking group and the axle of a rotaxane. Two-dimensional NMR analysis was

performed on the rotaxane–cation complexes in CDCl_3 . We found that the host rotaxanes transfer the perchlorate salts poorly when compared to B18C6, but they transfer chloride salts from 1 M salt solutions, whereas B18C6 does not. The transfer of chloride salts appears to rely on an allosteric type relationship between the binding of the chloride ion and metal cation to a rotaxane. Accordingly, when chloride binds to the dialkylammonium ion of the axle, the wheel moves along the axle and forms a binding site for a metal cation. In this report we demonstrate that host rotaxanes can bind metal cations, change their geometries upon cation and anion association, and operate through allosteric mechanisms, making them promising candidates for molecular devices.

- Copper-Catalyzed Direct Amination of Ortho-Functionalized Haloarenes with Sodium Azide as the Amino Source

Zhao, H.; Fu, H.; Qiao, R. *J. Org. Chem.* **2010**, *75*, 3311–3316.

Abstract:

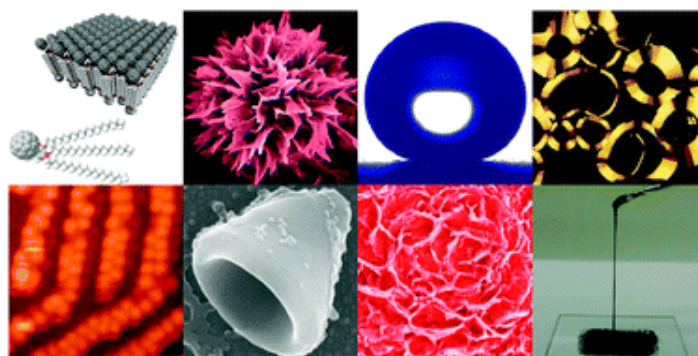


A simple copper-catalyzed direct amination of ortho-functionalized haloarenes (2-halobenzoic acid, 2-halobenzamide, and *N*-(2-bromophenyl)acetamide derivatives) has been developed with use of NaN_3 as the amino source in ethanol, and the corresponding ortho-functionalized aromatic amines were synthesized in good to excellent yields. The protocol undergoes one-pot Ullmann-type coupling of ortho-functionalized haloarenes with NaN_3 to lead to ortho-functionalized azidoarenes, followed by reduction with ethanol.

- Supramolecular soft and hard materials based on self-assembly algorithms of alkyl-conjugated fullerenes

Nakanishi, T. *Chem. Commun.* **2010**, *46*, 3425 – 3436.

Abstract:

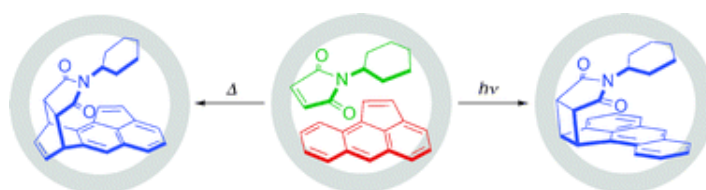


Dimensionally controlled and hierarchically assembled supramolecular architectures in nano/micro/bulk length scales are formed by self-organization of alkyl-conjugated fullerenes. The simple molecular design of covalently attaching hydrophobic long alkyl chains to fullerene (C_{60}) is different from the conventional (hydrophobic–hydrophilic) amphiphilic molecular designs. The two different units of the alkyl-conjugated C_{60} are incompatible but both are soluble in organic solvents. The van der Waals intermolecular forces among long hydrocarbon chains and the π – π interaction between C_{60} moieties govern the self-organization of the alkyl-conjugated C_{60} derivatives. A delicate balance between the π – π and van der Waals forces in the assemblies leads to a wide variety of

supramolecular architectures and paves the way for developing supramolecular soft materials possessing various morphologies and functions. For instance, superhydrophobic films, electron-transporting thermotropic liquid crystals and room-temperature liquids have been demonstrated. Furthermore, the unique morphologies of the assemblies can be utilised as a template for the fabrication of nanostructured metallic surfaces in a highly reproducible and sustainable way. The resulting metallic surfaces can serve as excellent active substrates for surface-enhanced Raman scattering (SERS) owing to their plasmon enhancing characteristics. The use of self-assembling supramolecular objects as a structural template to fabricate innovative well-defined metal nanomaterials links soft matter chemistry to hard matter sciences.

- Both [2+2] and [2+4] additions of inert aromatics *via* identical ternary host–guest complexes Horiuchi, S.; Nishioka, Y.; Murase, T.; Fujita, M. *Chem. Commun.* **2010**, 46, 3460 – 3462.

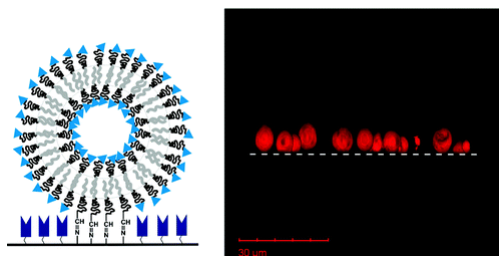
Abstract:



A self-assembled coordination cage enables inert aromatics to undergo both [2+2] and [2+4] cycloadditions by encapsulating them within the cavity. Aceanthrylene reacts with a maleimide derivative under thermal and photo-irradiation conditions to give a product as a single regio- and stereoisomer.

- Covalent Attachment of Polymersomes to Surfaces Domes, S.; Filiz, V.; Nitsche, J. ; Fromsdorf A.; Forster S. *Langmuir* **2010**, 26, 6927–6931.

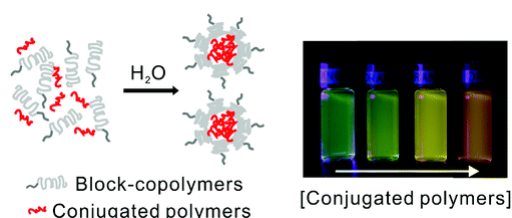
Abstract:



We show that vesicles made of block copolymers with aldehyde end groups can be covalently attached to aminated and non-aminated, untreated glass surfaces. The attached vesicles were sufficiently stable to allow a detailed investigation of vesicle shapes by confocal laser scanning microscopy (CLSM) and AFM in aqueous solutions allowing reconstruction of 3D images of the vesicle structure. Covalently attached PCL–PEO, PLA–PEO, and PI–PEO block copolymer vesicles have different footprint areas and different shapes due to their differences in bilayer stiffness.

- Encapsulating Light-Emitting Polymers in Block Copolymer Micelles Jung, Y.; Hickey, R. J.; Park, S.-J. *Langmuir* **2010**, 26, 7540–7543.

Abstract:

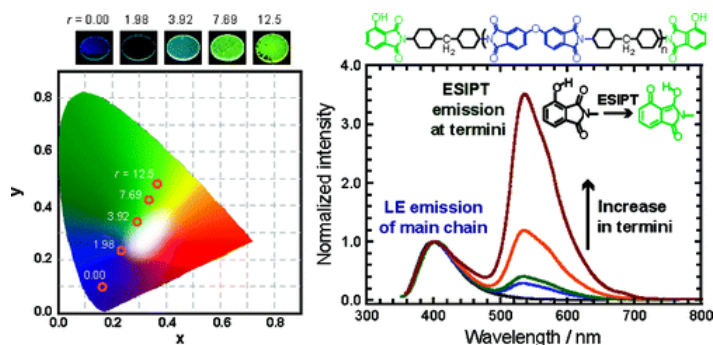


Conjugated polymers have excellent light-emitting properties that are useful for biological imaging and sensing applications. Here, we report a new way to form stable, water-soluble suspensions of conjugated polymers by encapsulating them in amphiphilic block copolymers. It was found that the folding property of conjugated polymers is a critical factor for solubilizing them into typical coil-coil block copolymer micelles. By introducing saturated bonds into conjugated polymers, they were readily encapsulated in block copolymer micelles, resulting in highly fluorescent polymer nanoparticles. The emission wavelength of fluorescent micelles can be tuned by controlling the number of encapsulated light-emitting polymers per micelle as well as changing the exciton delocalization length in conjugated polymers. This strategy has been extended to make multifunctional (i.e., fluorescent and magnetic) nanoparticles by encapsulating iron oxide nanoparticles in light-emitting polymers.

- Excited-State Intramolecular Proton Transfer in Imide Compounds and its Application to Control the Emission Colors of Highly Fluorescent Polyimides

Wakita, J.; Inoue, S.; Kawanishi, N.; Ando, S. *Macromolecules* **2010**, *43*, 3594–3605.

Abstract:



A new molecular design concept for colorless and multicolor light-emitting polyimides (PIs) based on excited-state proton transfer is proposed. The ultraviolet–visible optical absorption spectra and fluorescence spectra of PIs containing hydroxy groups in their anhydride moieties and their corresponding imide compounds were extensively investigated. *N*-Cyclohexyl-3-hydroxyphthalimide (3HNHPI), which forms intramolecular hydrogen bonding between the hydroxy group and imide carbonyl group, exhibited an excited-state intramolecular proton transfer (ESIPT) emission at 534 nm with excitation at 332 nm having a large Stokes' shift of 11394 cm^{-1} . The highly fluorescent PIs, prepared from 4,4'-oxidiphthalic dianhydride (ODPA) and 4,4'-diaminocyclohexylmethane (DCHM) end-capped with 3-hydroxyphthalic anhydride, are colorless and exhibited two characteristic fluorescence peaks at 400 and 530 nm with excitation at 340 nm. These PIs showed graded multicolor emission (blue, light-blue, white, and light-green) depending on the amount of fluorescent termini while maintaining colorless and transparency. It was clarified that ESIPT emission is a useful tool for controlling the absorption and fluorescence properties of PIs.

- Gilch and Horner–Wittig Routes to Poly(*p*-phenylenevinylene) Derivatives Incorporating Monoalkyl Defect-Free 9,9-Dialkyl-1,4-fluorenylene Units

Laughlin, B. J.; Smith, R. C. *Macromolecules* **2010**, *43*, 3744–3749.

Abstract:



A facile synthetic route allowed access to 1,4-dimethyl-9,9-dihexylfluorene (**3**) with no monoalkyl defects. Compound **3** was subsequently transformed to monomers for incorporation of 9,9-dihexyl-1,4-fluorenylene units into poly(*p*-phenylenevinylene) derivatives **P1** and **P2** via Horner–Wittig condensation and Gilch routes, respectively. The photophysical properties of **P1** and **P2** were characterized in solution and in solid state as thin films, and the robustness of film photophysical properties to thermal stress was evaluated. **P1** and **P2** appear to be the first π -conjugated polymers incorporating 9,9-dialkyl-1,4-fluorenylene units.