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**Drop-On-Drop Multimaterial 3D Bioprinting Realized by Peroxidase-Mediated Cross-Linking**

A cytocompatible inkjet bioprinting approach that enables the use of a variety of bioinks to produce hydrogels with a wide range of characteristics is developed. Stabilization of bioinks is caused by horseradish peroxidase (HRP)-catalyzed cross-linking consuming hydrogen peroxide (H2O2). 3D cell-laden hydrogels are fabricated by the sequential dropping of a bioink containing polymer(s) cross-linkable through the enzymatic reaction and H2O2 onto droplets of another bioink containing the polymer, HRP, and cells. The ≈95% viability of enclosed mouse fibroblasts and subsequent elongation of the cells in a bioprinted hydrogel consisting of gelatin and hyaluronic acid derivatives suggest the high cytocompatibility of the developed printing approach. The existence of numerous polymers, including derivatives of polysaccharides, proteins, and synthetic polymers, cross-linkable through the HRP-catalyzed reaction, means the current approach shows great promise for biofabrication of functional and structurally complex tissues. Bioprinting through drop-on-drop inkjetting and horseradish peroxidase-catalyzed cross-linking is cytocompatible and enables the use of a variety of bioinks to develop functional 3D hydrogel constructs tailored for individual applications. This approach opens new avenues for tissue engineering and regenerative medicine based on bioprinting.

**Reducing Trap-Assisted Recombination in Small Organic Molecule-Based Photovoltaics by the Addition of a Conjugated Block Copolymer**

The performance of organic photovoltaics (OPVs) based on the small-molecule organic semiconductor p-DTS(FBTTh2)2 is greatly improved by the addition of a conjugated block copolymer composed of difluoroquinoxaline and thienopyrrolo dine blocks (D130). The power conversion efficiency (PCE) of the p-DTS(FBTTh2)2-based OPV is improved from 5.08% to 6.75% by the addition of 5 wt% D130 to the photoactive layer, which is composed of p-DTS(FBTTh2)2 and a fullerene derivative. Current–voltage and grazing incidence wide-angle X-ray scattering analyses revealed that the addition of D130 significantly reduces the trap density of the device and changes the packing orientation of p-DTS(FBTTh2)2 from mostly edge-on to partially face-on. These changes greatly improve the charge carrier mobility of the OPV, indicating that D130 is highly compatible with p-DTS(FBTTh2)2. Furthermore, the addition of D130 improve the photostability of the OPV by reducing the burn-in loss under a light soaking intensity of 1 sun. The D130-based OPV maintained 34% of its initial PCE after a light soaking test for 858 h. In contrast, the PCE of the OPV without D130 reduced to 14% of its initial efficiency in the same time period. The performance of small-molecule-based organic photovoltaics is greatly improved by the addition of a conjugated block copolymer composed of difluoroquinoxaline and thienopyrrolo dine blocks (D130). It is revealed that the addition of D130 significantly reduced the trap density of the device. In addition, the photostability of the device is significantly enhanced by the incorporation of D130.

**Synergistic Effects of Selenophene and Extended Ladder-Type Donor Units for Efficient Polymer Solar Cells**

Two pairs of polymer donor materials based on indacenodithiophene (IDT) and indacenodithieno[3,2-b]thiophene (IDTT) as the donor units are synthesized. Thiophene or selenophene is introduced as the π-bridge units and electron-deficient fluorine-substituted quinoxaline is used as acceptor unit. Selenophene-containing polymers PIDT-DFQ-Se and PIDTT-DFQ-Se show redshifted absorption and narrower bandgaps. Combined with IDTT donor unit, PIDTT-DFQ-Se shows the highest absorption coefficient. Both the IDTT unit and selenophene unit have positive effects on the hole mobilities, making PIDTT-DFQ-Se the highest one. The best power conversion efficiency of 7.4% is obtained from devices based on PIDTT-DFQ-Se:[6,6]-phenyl C71 butyric acid methyl ester (PC71BM) with a Jsc of 12.6 mA cm−2, a Voc of 0.89 V, and a fill factor (FF) of 0.66. Two pairs of electron donor polymer
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Materials with fused-ring indacenodithiophene (IDT) or indacenodithieno[3,2-b]thiophene (IDTT) as donor units bridged with thiophene or selenophene are synthesized. The best power conversion efficiency of 7.4% is obtained from devices fabricated from PIDTT-DFQ-Se:PC71BM due to the synergetic effect of extended IDTT unit and bridged selenophene, resulting in the higher absorption coefficient and mobilities.

Understanding the Impact of Film Disorder and Local Surface Potential in Ultraviolet Photoelectron Spectroscopy of PEDOT

The spectra of conducting polymers obtained using ultraviolet photoelectron spectroscopy (UPS) exhibit a typical broadening of the tail \( \Delta \text{UPS} \approx 1 \text{ eV} \), which by an order of magnitude exceeds a commonly accepted value of the broadening of the tail of the density of states \( \Delta \text{DOS} \approx 0.1 \text{ eV} \) obtained using transport measurements. In this work, an origin of this anomalous broadening of the tail of the UPS spectra in a doped conducting polymer, PEDOT (poly(3,4-ethylenedioxythiophene)), is discussed. Based on the semiempirical approach and using a realistic morphological model, the density of valence states in PEDOT doped with molecular counterions is computed. It is shown that due to a disordered character of the material with randomly distributed counterions, the localized charge carriers in PEDOT crystallites experience spatially varying electrostatic potential. This leads to spatially varying local vacuum levels and binding energies. Taking this variation into account the UPS spectrum is obtained with the broadening of the tail comparable to the experimentally observed one. The results imply that the observed broadening of the tail of the UPS spectra in PEDOT provides information about a disordered spatially varying potential in the material rather than the broadening of the DOS itself. A pronounced discrepancy of the broadening of the tail of the density of states of a doped conducting polymer, (poly(3,4-ethylenedioxythiophene)), extracted from the respective ultraviolet photoelectron spectroscopy and transport measurements, is discussed and attributed to the effect of spatially varying local vacuum levels and binding energies caused by disorder (randomly distributed counterions).

Enhanced Fluorescence Properties of Stilbene-Containing Alternating Copolymers

In recent years, nonconjugated, fluorophore-free organic polymers have emerged as potentially useful light-emitting materials. The fluorescence properties of a novel class of nonconjugated, tert-butyl carboxylate functionalized stilbene-containing alternating copolymers are investigated in this work. These sterically crowded, semi-rigid copolymers exhibit very strong blue fluorescence in organic solvents upon irradiation. The origin of the fluorescent band with high quantum yield is attributed to the “through space” \( \pi-\pi \) interactions between the phenyl rings from the stilbene and CO groups from the anhydride groups. To the best of our knowledge, the di-tert-butyl group-containing stilbene and maleic anhydride alternating copolymer showed one of the highest fluorescent intensities among all fluorophore-free polymers. The excellent linearity of the luminescence property of this copolymer is an important attribute for future potential quantitative applications. The fluorescence is maintained when the tert-butyl groups are removed and the resulting carboxylic acid-functionalized copolymer is dissolved in water at neutral pH, which can render these copolymers as attractive candidates for diagnostic and therapeutic applications. Nonconjugated, tert-butyl carboxylate functionalized stilbene-containing alternating copolymers exhibit strong fluorescence with excellent linearity. The origin of the fluorescence is attributed to the “through space” \( \pi-\pi \) interactions between the phenyl rings from the stilbene and CO groups from the anhydride. The fluorescence is maintained when the tert-butyl groups are removed and the resulting carboxylic-acid-functionalized copolymer is dissolved in water at neutral pH.

Thermally Labile Self-Healable Branched Gel Networks Fabricated by New Macromolecular Engineering Approach Utilizing Thermoreversibility
A new approach based on macromolecular engineering through thermoreversibility is reported to fabricate the engineered gel networks of thermally labile branched polymers exhibiting robust self-healing. This approach centers on the synthesis of linear polymers having Diels–Alder cycloadducts in the backbones (DALPs) through A2 + B2 step-growth polymerization of a difunctional furan and a difunctional maleimide. Reactive mixtures of the resulting DALP with a polyfuran at elevated temperature allow for the formation of engineered gel networks through random dissociation of backbone DA linkages of the DALPs by retro-Diels–Alder reaction, followed by their reconstruction in the presence of polyfuran (with functionality > 2) by Diels–Alder reaction. Optimizing the ratio of furan to DA linkages in the reactive mixtures yields thermally labile networks exhibiting excellent thermoreversibility. Effective self-healing demonstrated with reconstruction from two separate pieces and complete void filling on surface cuts as well as recovery of healing viscoelasticity suggest that the new macromolecular engineering approach offers versatility toward the development of thermally mendable thermosets. A new approach is designed based on macromolecular engineering through thermoreversibility of linear polymers having Diels–Alder cycloadducts reacting with polyfurans at elevated temperature. This enables the fabrication of engineered gel networks of thermally labile branched polymers exhibiting robust self-healing, thus offering the versatility toward the development of thermally mendable thermosets.

**Custom 3D Printable Silicones with Tunable Stiffness**

Silicone elastomers have broad versatility within a variety of potential advanced materials applications, such as soft robotics, biomedical devices, and metamaterials. A series of custom 3D printable silicone inks with tunable stiffness is developed, formulated, and characterized. The silicone inks exhibit excellent rheological behavior for 3D printing, as observed from the printing of porous structures with controlled architectures. Herein, the capability to tune the stiffness of printable silicone materials via careful control over the chemistry, network formation, and crosslink density of the ink formulations in order to overcome the challenging interplay between ink development, post-processing, material properties, and performance is demonstrated. The capability to tune the stiffness of 3D printable silicone materials via careful control over the chemistry, network formation, and crosslink density of our ink formulations is demonstrated in order to overcome the challenging balance between ink development, post-processing, material properties, and performance. Material applications include high-performance foams and cellular solids, soft robots, biomedical devices and biological scaffolds, and flexible and stretchable electronics.

**Ultrahigh Flux Composite Hollow Fiber Membrane via Highly Crosslinked PDMS for Recovery of Hydrocarbons: Propane and Propene**

In order to make membrane separation technologies more cost-competitive with the well-established processes that are energy intensive for gas/vapor separation, a defect-free membrane with a high gas permeance is necessary. However, it remains challenging to meet these needs because of the difficulties in developing a suitable material and process that are economical and practical. Herein, a novel and straightforward strategy is presented to produce a defect-free hollow fiber composite membrane using a highly crosslinked polydimethylsiloxane (PDMS) synthesized by using a postcrosslinking method. The PDMS can be directly coated on a polyacrylonitrile (PAN) membrane substrate, and the resultant PDMS/PAN composite membrane has ultrahigh C3H8 and C3H6 permeances that are higher than 10 000 and 11 000 GPU, respectively, and the corresponding permselectivity of C3H8/N2 and C3H6/N2 are about 21 and 24, respectively. The newly developed methods and materials may open up a new cost-effective method to fabricate next-generation composite membranes for the recovery of hydrocarbons, organic vapors, and gases. A highly crosslinked polydimethylsiloxane (PDMS) can be synthesized via a thermal-crosslinking method followed by a postcrosslinking process. The PDMS (Mn = 577 kg mol⁻¹) can be
directly coated on a polyacrylonitrile (PAN) membrane substrate, and the resultant PDMS/PAN composite membrane is defect-free and has ultrahigh C3H8 and C3H6 permeances that are higher than 10 000 and 11 000 GPU, respectively.

Multicompartiment Vesicles Formation by Emulsification-Induced Assembly of Poly(ethylene oxide)-block-poly(ε-caprolactone) and Their Dual-Loading Capability

Emulsification-induced assembly is employed to allow structural diversity in nanoaggregates of a biocompatible amphiphilic polymer, poly(ethylene oxide)-block-poly(ε-caprolactone). Onion-like vesicles are efficiently produced by tuning the interfacial instability of the oil-in-water emulsion. The increase in the polymer concentration and use of the organic solvents with a low interfacial tension between water and the oil phase lead to a strong tendency of emulsion droplets to generate the onion-like vesicles. The vesicular networks and fibers are also obtained by controlling the concentration and type of the surfactant, respectively. Interestingly, the onion-like vesicles composed of alternating walls and water channels and the vesicular networks originated from a string of vesicles show dual-loading ability for hydrophobic and hydrophilic dyes but slightly different loading capacities. This result indicates that the development of a methodology to fabricate well-defined, unique nanostructures, such as multivesicular and multilamellar nanostructures, and subsequent elucidation of their structure–property relationships can provide useful guidance in the design of novel biomedical materials. Multicompartiment vesicles, including onion-like vesicles and vesicular networks, are constructed by tuning the interfacial instability of an oil-in-water emulsion of a single-polymer molecular scaffold. The dual-loading ability for hydrophobic and hydrophilic dyes is demonstrated with different loading capacities due to the spatial organization of each compartment constituting the onion-like vesicles and vesicular networks.

4D Printed Actuators with Soft-Robotic Functions

Soft matter elements undergoing programed, reversible shape change can contribute to fundamental advance in areas such as optics, medicine, microfluidics, and robotics. Crosslinked liquid crystalline polymers have demonstrated huge potential to implement soft responsive elements; however, the complexity and size of the actuators are limited by the current dominant thin-film geometry processing toolbox. Using 3D printing, stimuli-responsive liquid crystalline elastomeric structures are created here. The printing process prescribes a reversible shape-morphing behavior, offering a new paradigm for active polymer system preparation. The additive character of this technology also leads to unprecedented geometries, complex functions, and sizes beyond those of typical thin-films. The fundamental concepts and devices presented therefore overcome the current limitations of actuation energy available from thin-films, thereby narrowing the gap between materials and practical applications. 3D printing is used to create stimuli-responsive liquid crystalline elastomeric structures. Printing prescribes the reversible shape-morphing behavior of the structures, leading to intricate geometries, complex functions, and sizes beyond those fabricated using the current dominant thin-film geometry processing toolbox. This technology opens new avenues for the development of new shape-morphing architectures for medicine, microfluidics, adaptive optics, haptics, or soft robotics.

Supramolecular “Step Polymerization” of Preassembled Micelles: A Study of “Polymerization” Kinetics

In nature, sophisticated functional materials are created through hierarchical self-assembly of nanoscale motifs, which has inspired the fabrication of man-made materials with complex architectures for a variety of applications. Herein, a kinetic study on the self-assembly of spindle-like micelles preassembled from polypeptide graft copolymers is reported. The addition of dimethylformamide and, subsequently, a selective solvent (water) can generate a “reactive point” at both ends of the spindles as a
result of the existence of structural defects, which induces the “polymerization” of the spindles into nanowires. Experimental results combined with dissipative particle dynamics simulations show that the polymerization of the micellar subunits follows a step-growth polymerization mechanism with a second-order reaction characteristic. The assembly rate of the micelles is dependent on the subunit concentration and on the activity of the reactive points. The present work reveals a law governing the self-assembly kinetics of micelles with structural defects and opens the door for the construction of hierarchical structures with a controllable size through supramolecular step polymerization. Preassembled micelles are found to be able to end-to-end “polymerize” into 1D hierarchical nanowires. Experimental results combined with dissipative particle dynamics simulations show that the polymerization kinetics follow a step-growth polymerization mechanism with a second-order reaction characteristic. The assembly rate of the micelles can be adjusted by the subunit concentration and the solvent condition.

Stretchable Fluorescent Polyfluorene/Acrylonitrile Butadiene Rubber Blend Electrospun Fibers through Physical Interaction and Geometrical Confinement

Stretchable light-emitting polymers are important for wearable electronics; however, the development of intrinsic stretchable light-emitting materials with great performance under large applied strain is the most critical challenge. Herein, this study demonstrates the fabrication of stretchable fluorescent poly[(9,9-bis(3-((N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctyl-fluorene))]/acrylonitrile butadiene rubber (PFN/NBR) blend nanofibers using the uniaxial electrospinning technique. The physical interaction of PFN with NBR and the geometrical confinement of nanofibers are employed to reduce PFN aggregation, leading to the high photoluminescence quantum yield of 35.7%. Such fiber mat film shows stable blue emission at the 50% strain for 200 stretching/release cycles, which has potential applications in smart textiles. Stretchable fluorescent materials are highly desired for wearable electronics. Herein, the fabrication of fluorescent poly[(9,9-bis(3-((N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctyl-fluorene))]/acrylonitrile butadiene rubber (PFN/NBR) electrospun nanofibers under stretching is demonstrated. The physical interaction of PFN with NBR and the geometric confinement of nanofibers effectively reduced PFN aggregation, leading to the high photoluminescence quantum yield of 35.7% and stable blue-emission under 50% strain.

Functional Polymer Opals and Porous Materials by Shear-Induced Assembly of Tailor-Made Particles

Photonic band-gap materials attract enormous attention as potential candidates for a steadily increasing variety of applications. Based on the preparation of easily scalable monodisperse colloids, such optically attractive photonic materials can be prepared by an inexpensive and convenient bottom-up process. Artificial polymer opals can be prepared by shear-induced assembly of core/shell particles, yielding reversibly stretch-tunable materials with intriguing structural colors. This feature article highlights recent developments of core/shell particle design and shear-induced opal formation with focus on the combination of hard and soft materials as well as crosslinking strategies. Structure formation of opal materials relies on both the tailored core/shell architecture and the parameters for polymer processing. The emphasis of this feature article is on elucidating the particle design and incorporation of addressable moieties, i.e., stimuli-responsive polymers as well as elaborated crosslinking strategies for the preparation of smart (inverse) opal films, inorganic/organic opals, and ceramic precursors by shear-induced ordering. Stimuli-responsive photonic materials have attracted enormous attention for a huge range of recent polymer-based applications. This feature article focuses on the preparation of ordered core/shell particles by shear-induced particle assembly. Some recent advances for elastomeric opal film formation and the design of smart optical sensors, inverse opals, porous ceramics, and carbonaceous structures are highlighted.
Proton Conducting Membranes Based on Poly(Ionic Liquids) Having Phosphonium Counter-Cations

Proton conducting polymeric membranes are highly searched in many different technologies ranging from energy to biosensing. Protic ionic liquids and their polymeric version represent a new family of proton conducting molecules with relatively facile synthesis and excellent properties. In this work, protic poly(ionic liquids) having the most popular phosphonium counter-cations are presented for the first time. The synthesis is carried out through proton transfer reactions or through ion exchange reactions by using commercially available tertiary phosphines. Tributyl-, trioctyl-, and tricyclohexylphosphine are selected to form the desired cations. Polystyrene sulfonic acid, poly(2-acrylamido-2-methyl-1-propanesulfonic acid), and lithium poly[(4-styrenesulfonyl)(trifluoromethanesulfonyl)imide] polymers are used to form the polymeric anions. The chemical structure of the protic poly(ionic liquids) is confirmed by spectroscopic characterizations such as Fourier transform infrared and nuclear magnetic resonance spectroscopies. Thermal properties of the polymer are characterized by means of differential scanning calorimetry and thermogravimetric analysis. Polymers exhibit good membrane forming ability as well as high ionic conductivities in the range of 10−8 to 10−3 S cm−1 from 30 to 90 °C. A variety of new protic phosphonium-based poly(ionic liquids) are synthesized, and clear standing films are prepared. Among all the three polymer chains and the three phosphonium cations studied, it is found that the couple of poly[(4-styrenesulfonyl)(trifluoromethanesulfonyl)imide] and HP+444 exhibits the best comprehensive performance. The “dry” ionic conductivity reaches 2 × 10−4 S cm−1 at 150 °C.

Reversible Modulation of Elasticity in Fluoroazobenzene-Containing Hydrogels Using Green and Blue Light

Hydrogels are soft materials that have found multiple applications in biomedicine and represent a good platform for the introduction of molecular switches and synthetic machines into macromolecular networks. Tuning their mechanical properties reversibly with light is appealing for a variety of advanced applications and has been demonstrated in the past; however, their activation typically requires the use of UV light, which displays several drawbacks related to its damaging character and limited penetration in tissues and materials. This study circumvents this limitation by introducing all-visible ortho-fluoroazobenzene switches into a hydrophilic network, which, as a result, can be activated with green or blue light. Photoisomerization of the photochromic moieties is accompanied by a reversible tuning of the elastic modulus. The translation of molecular isomerization within the network into macroscopic modulation of its mechanical properties is attributed to different aggregation tendencies of the E and Z isomers of the azobenzene derivatives. Phototuning hydrogels’ mechanical properties with visible light is achieved by incorporating all-visible azobenzene derivatives within PEGylated networks.

Copper(0) Mediated Single Electron Transfer Controlled Radical Polymerization toward CF Bonds on Poly(vinylidene fluoride)

The first copper(0) mediated controlled radical polymerization (CRP) of methyl methacrylate (MMA) toward CF bonds onto poly(vinylidene fluoride) (PVDF) is reported with rather high activity. By avoiding the halogen exchange, Cu0 instead of CuI complexes utilized as catalyst is responsible for the significantly improved polymerization activity. Using FH decoupled nuclear magnetic resonance technique, the grafting sites onto PVDF are finely located. From this, detailed topologic information including the grafting density, average length of each side chain, along with the overall grafted content of PMMA, is detected by tracking the polymerization as a function of time. This work offers not only a facile CRP strategy based on inactive CF bonds but also a deep insight into the cleavage of F-bearing compounds in organic chemistry. The first copper(0) mediated controlled radical polymerization of
methyl methacrylate toward CF bonds onto poly(vinylidene fluoride) (PVDF) with rather high activity is reported. This method may provide a facile strategy to prepare PVDF-based graft copolymers.

**Kinetics of Thermal Polymerization Can Be Studied during Continuous Cooling**

It is demonstrated that differential scanning calorimetry can measure the kinetics of the thermally initiated polymerization during continuous cooling. The measurements are accomplished by switching from fast heating to much slower cooling. The study is exemplified by crosslinking polymerization (curing) of diglycidyl ether of bisphenol A epoxy and m-phenylenediamine taken in stoichiometric and nonstoichiometric ratios and measured under heating and cooling conditions. An advanced isoconversional method reveals that the reaction in the nonstoichiometric system follows the kinetics of the single-step type. Its activation energy is constant and the same for heating and cooling conditions. The stoichiometric system exhibits the multistep kinetics characterized by the dependencies of the activation energy on temperature that differ qualitatively for cooling and heating runs. The discovered differences emphasize the need for further systematic studies of the thermal polymerization during continuous cooling. Differential scanning calorimetry (DSC) can measure the kinetics of the thermally initiated polymerization during continuous cooling. Analysis of DSC data on crosslinking epoxy-amine polymerization by an isoconversional method has revealed qualitatively different dependencies of the activation energy on temperature for heating and cooling conditions. This result emphasizes the need for systematic studies of the thermal polymerization during continuous cooling.

**Broadening the Photoresponse to Near-Infrared Region by Cooperating Fullerene and Nonfullerene Acceptors for High Performance Ternary Polymer Solar Cells**

Ternary polymer solar cells (PSCs) based on multiple materials with level matching and complementary absorptions are regarded as an efficient way to overcome the light-harvesting restriction to surpass high-performance binary PSCs. This study introduces the third component, nonfullerene acceptor IEICO, into binary PSC-based PBDTBDD:PC71BM to fabricate ternary PSC with one donor and two acceptors. By carefully tuning the third component ratio and cathode engineering, the resulting ternary PSC shows a power conversion efficiency of 10.51%, greatly improved in comparison with binary PSCs-based PBDTBDD:PC71BM (7.86%) and PBDTBDD:IEICO (5.19%). In addition to extended light absorption, the third component IEICO could accelerate charge-carrier transfer, decrease charge recombination, and increase electron collection, resulting from cascade energy levels, and ameliorate the device morphology to increase the contact area of the active layer and cathode buffer layer. This work demonstrates that ternary PSC incorporated with IEICO is a promising structure for producing high performance PSCs. Efficient ternary polymer solar cells are demonstrated by cooperating fullerene and nonfullerene acceptors to extend the photoresponse to the near-infrared region. A promising power conversion efficiency of 10.51% is achieved for ternary PSCs-based PBDTBDD:PC71BM:IEICO.

**Homo- and Copolycyclotrimerization of Aromatic Internal Diynes Catalyzed with Co2(CO)8: A Facile Route to Microporous Photoluminescent Polyphenylenes with Hyperbranched or Crosslinked Architecture**

This study reports the first Co2(CO)8-catalyzed [2+2+2] polycyclotrimerization by the transformation of internal ethynyl groups of aromatic diyne monomers. The reaction yields polycyclotrimers of polyphenylene-type with either hyperbranched or partly crosslinked architecture. The homopolycyclotrimerization of the monomers with two ethynyl groups per one molecule, namely 1,4-bis(phenylethynyl)benzene, 4,4?-bis(phenylethynyl)biphenyl, and 4-(phenylethynyl)phenylacetylene, gives partly crosslinked, insoluble polyphenylenes. The soluble, hyperbranched polyphenylenes are generated via copolycyclotrimerization of 1,4-bis(phenylethynyl)benzene with 1,2-diphenylacetylene (average number of ethynyl groups per
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This one-step polycyclotrimerization path to hyperbranched or partly crosslinked polyphenylenes is an alternative to the synthesis of these polymers by Diels–Alder transformation of substituted cyclopentadienones. All polyphenylenes prepared exhibit photoluminescence with emission maxima ranging from 381 to 495 nm. Polyphenylenes with a less compact packing of segments are microporous (specific surface area up to 159 m² g⁻¹), which is particularly important in the case of soluble polyphenylenes because they can be potentially used to prepare microporous layers. The Co₂(CO)₈-catalyzed [2+2+2] polycyclotrimerization proceeding through transformation of internal ethynyl groups of aromatic diyne monomers is reported for the first time. The reaction yields polyphenylene-type polycyclotrimers with tunable hyperbranched or partly crosslinked architecture. The microporosity and photoluminescence of the polyphenylenes prepared are governed by the compactness of their structure.

Spatial Patterning of Hydrogels via 3D Covalent Transfer Stamping from a Fugitive Ink

In this study, a novel hydrogel patterning approach using 3D covalent transfer stamping from a fugitive ink is introduced. A model transfer molecule (7-diethylamino-3-(4-maleimidylphenyl)-4-methylcoumarin (CPM)) is absorbed into a 3D fugitive ink stamp made from poly(caprolactone), and then encapsulated in a poly(ethylene glycol) hydrogel. As the CPM diffuses from the fugitive ink to the curing hydrogel it is selectively covalently bound at the boundary of the ink and the hydrogel. Removal of the fugitive ink by solvent exchange leads to a negative copy of interconnected channels patterned with the localized transfer of the molecules at the hydrogel interface. The results suggest that small molecules can be patterned in porous hydrogels in a spatially controllable manner and that the transferred amount can be tuned. A novel hydrogel patterning approach using 3D covalent transfer stamping from a fugitive ink is introduced. A model transfer molecule is selectively covalently bound at the boundary of the ink and the hydrogel. This work allows the creation of hydrogels with architecture not possible using other techniques with small molecules patterned onto only the channel walls.