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COVER PICTURE



The cover image shows the hydrogen-storage capacity of a Li-decorated (0,6) boron nanotube, which is obtained by rolling up a boron-double-ring sheet. On p. 3453, Y. Liu et al. describe the use of density functional theory to reveal several novel boron nanostructures based on the boron double ring.

NEWS

Spotlights on our sister journals

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Further masthead information follows directly after the Table of Contents.

CONCEPTS

You can print anything these days: A simple and general solvent exchange technology is introduced for inkjet printing of 2D layered materials. The technology addresses the critical challenges and improves the manufacturing efficiency and product quality. Excellent jetting performance, ideal printing patterns and a variety of promising applications for inkjet printing of 2D layered materials are demonstrated.



J. Li,* M. C. Lemme, M. Östling

3427 - 3434

Inkjet Printing of 2D Layered Materials

COMMUNICATIONS

Well gel: Oleogels (containing > 97 wt% liquid oil) are prepared by using a polysaccharide-based emulsion as a template. The obtained oleogel has a unique microstructure and interesting rheological properties, including a high gel strength, shear sensitivity, good thixotropic recovery, and good thermostability.



A. R. Patel,* N. Cludts, M. D. Bin Sintang, B. Lewille, A. Lesaffer, K. Dewettinck

3435 - 3439

Polysaccharide-Based Oleogels Prepared with an Emulsion-Templated Approach

Inside Cover



Fatal attraction: Size-controlled Fe_2O_3 nanoparticles grown in a nanoporous carbon material with tuneable pore diameters are prepared and exhibit strong, non-linear magnetic properties and an extremely high magnetic moment of approximately 229 emu g⁻¹.



S. Alam, C. Anand, K. S. Lakhi, J.-H. Choy, W. S. Cha, A. Elzhatry, S. S. Al-deyab, Y. Ohya, A. Vinu*

3440 - 3443

Highly Magnetic Nanoporous Carbon/

A bead cluster biomarker probe uses fractal dimension analysis to quantitate marker concentration for medical diagnostics (see picture).



A. Hecht, P. Commiskey, F. Lazaridis, P. Argyrakis,* R. Kopelman*

3444 - 3446

Fractal Dimension of Microbead Assemblies Used for Protein Detection

C. M. Winterflood,* H. Ewers*

3447 - 3451

Single-Molecule Localization Microscopy using mCherry



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The cherry on top! Single-molecule localization microscopy using standard mCherry is shown with sub-40 nm resolution. The wealth of well-characterized mCherry fusion proteins can be readily revisited by using single-molecule super-resolution microscopy. Super-resolution imaging can be done in a straightforward way eliminating the need for external labeling or the use of highlighter fluorescent proteins.

ARTICLES

J. Wang, H.-Y. Zhao, Y. Liu*

3453 - 3459

Boron-Double-Ring Sheet, Fullerene, and Nanotubes: Potential Hydrogen Storage Materials



Front Cover

S. O. Krabbenborg, J. van Weerd, M. Karperien,* P. Jonkheijm,* J. Huskens*

3460 - 3465

Locked-in Biomimetic Surface Gradients that are Tunable in Size, Density and Functionalization



Inside Back Cover

F. C. Maier, M. Fyta*

3466 - 3475

Type-Dependent Identification of DNA Nucleobases by Using Diamondoids



Back Cover



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The new graphene: Similar to carbonbased graphene, fullerenes, and carbon nanotubes, boron atoms can form sheets, fullerenes, and nanotubes. Here, several of these novel boron structures—all based on the boron double ring—are investigated. The nanostructures are interesting potential candidates for hydrogen storage.



Locked-in supported lipid bilayer gradients are prepared that can be tuned in space, time and density in a process controlling lipid phase behaviour, electric field and temperature. Stable gradients of functional serine and biotin terminated lipids are shown. Covalent and non-covalent chemical modification is used to fabricate gradients of FITC, hexahistidine-tagged proteins and SAv/ biotin.

Diamondoid biosensor: Diamondoids, small amine-modified diamond-like cages, can probe DNA molecules and identify the type (purine or pyrimidine) of nucleobase. Diamondoids can potentially be used to functionalize a biosensing device, scan along the DNA, and, based on the specific frontier orbitals as shown in the figure, read out the DNA nucleobases.

Anything but sunblock: Triphenylamine groups give a good blocking effect in phenoxazine dyes for cobalt electrolyte-based dye-sensitized solar cells.



Y. Hao, H. Tian, J. Cong, W. Yang, I. Bora, L. Sun, G. Boschloo,* A. Hagfeldt

3476 - 3483

Triphenylamine Groups Improve Blocking Behavior of Phenoxazine Dyes in Cobalt-Electrolyte-Based Dye-Sensitized Solar Cells

Ground control to Major Tom: Global control over the self-assembly of tetraundecyl metal porphyrins into a monolayer at a solid/liquid interface is governed by the concentration and composition of the supernatant solution. Subsequent manipulation by nanoshaving with a scanning tunneling microscopy tip creates monolayer defects, which can mediate a decrease or increase in local surface density, or the insertion of a second species of the same shape.

More flux, better signal! In an imaging photoelectron photoion coincidence study (iPEPICO) the two isomeric C₉H₇ radicals, 1-phenylpropargyl (1PPR) and 3-phenylpropargyl (3PPR), are reinvestigated, and improved ionization energies and threshold photoelectron spectra are obtained.



M. J. J. Coenen, T. Khoury, M. J. Crossley, B. L. M. Hendriksen, J. A. A. W. Elemans,* S. Speller

3484 - 3488

Nanostructuring of Self-Assembled Porphyrin Networks at a Solid/Liquid Interface: Local Manipulation under Global Control



F. Holzmeier, M. Lang, P. Hemberger,* I. Fischer*

3489 - 3492

Improved Ionization Energies for the Two Isomers of Phenylpropargyl Radical

Heterocyclic spiropentanes: The strain and relative stability of heterocyclic spiro[2.2]pentane cations with N, P, and As as spiro atoms are studied theoretically. In addition, their interaction with the chloride and 3-boranuidaspiro-[2.2]pentane anions (see picture) are investigated.



C. Trujillo, G. Sánchez-Sanz,* I. Alkorta, J. Elguero

3493 – 3501

A Computational Study on 3-Azonia-, 3-Phosphonia-, and 3-Arsoniaspiro[2.2]pentanes and Related Three-Membered Heterocycles

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B. Maity, A. Chatterjee, S. A. Ahmed, D. Seth*

3502 - 3514

Supramolecular Interactions of Nonsteroidal Anti-inflammatory Drug in Nanochannels of Molecular Containers: A Spectroscopic, Thermogravimetric and Microscopic Investigation S4800 10 KW 9 7mm x11 0k SptM

Be my guest! Supramolecular host– guest complexation between the nonsteroidal anti-inflammatory drug indomethacin and the nanochannels of different cyclodextrin molecular containers were investigated.

P. Giridhar, B. Weidenfeller, S. Zein El Abedin, F. Endres*

3515 - 3522

Electrodeposition and Magnetic Characterization of Iron and Iron– Silicon Alloys from the Ionic Liquid 1-Butyl-1-methylpyrrolidinium Trifluoromethylsulfonate



Knocking down the wall: Cyclic voltammetry of $FeCl_2 + SiCl_4$ in $[Py_{1,4}]TfO$ is performed, and an investigation into the microstructure and magnetic properties of electrodeposited FeSi alloys is presented.

L. Pengxia, Z. Du, D. Wang,* Z. Yang,* H. Sheng, S. Liang, H. Cao, W. He, H. Yang*

3523 - 3529

 Optoelectronic and Self-assembly Properties of Porphyrin Derivatives with Click Chemistry Modification



A series of functionalized porphyrin molecules containing electron-rich alkynes, synthesized by means of the Sonogashira coupling reaction, are further modified by reacting the ethynyl groups with click reagents through a formal [2+2] click reaction. Through a phaseexchange self-assembly method, highly organized morphologies are observed by scanning electron microscopy.

F. Chen,* H. Zhu, M. Forsyth

3530 - 3535

Modelling Ion-Pair Geometries and Dynamics in a 1-Ethyl-1methylpyrrolidinium-Based Ion-Conductive Crystal



Going through the motions: Temperature-dependent cation motions are predicted in different plastic crystals phases (see picture). Pseudorotation in the pyrrolidine ring is first expected to involve a phase IV to III transition. The partial rotation from one local minimum to another presents next-level dynamics. The free rotation of the cation is activated as the temperature increases, which may be accompanied by reorientation of the ethyl group.

Pick and choose: The selective extraction of metals from aqueous mixtures has generally relied on the use of selective ionophores. An alternative strategy is presented that exploits a recently developed approach to extraction into an ionic liquid phase, and shows that a high degree of control over selectivity can be obtained by tuning the relative concentrations of extraction agents.



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C. H. C. Janssen, A. Sánchez, M. N. Kobrak*

3536 - 3543

Selective Extraction of Metal lons from Aqueous Phase to Ionic Liquids: A Novel Thermodynamic Approach to Separations



[C_mim][C_SO_] Micelles - Mixed Micelles Vesion

In a jiffy! Spontaneous micelle-vesicle transitions in a mixed surface-active ionic-liquid system are of interest, because of the advantageous properties of amphiphilic ionic liquids compared with conventional surfactants. In addition to detailed characterization, how ultrafast fluorescence resonance energy transfer (FRET) can be used to probe such transitions is discussed.

S. Mandal, J. Kuchlyan, D. Banik, S. Ghosh, C. Banerjee, V. Khorwal, N. Sarkar*

3544 - 3553

Ultrafast FRET to Study Spontaneous Micelle-to-Vesicle Transitions in an Aqueous Mixed Surface-Active Ionic-Liquid System



A noble cause: The stability of noble gas (Ng)-bound SiH_3^+ clusters is explored by ab initio computations. SiH_3^+ can bind Ng atoms effectively. The Si–Xe/Rn bonds are covalent in nature.



Both the -I (inductive) effect of the X atoms and X \rightarrow Si π -backbonding have decisive roles in the Ng binding ability of SiX₃⁺ (X = F, Cl, Br).

S. Pan, D. Moreno, G. Merino,* P. K. Chattaraj*

3554 - 3564

Stability of Noble-Gas-Bound SiH₃⁺ Clusters

Illuminating mechanoluminescence: Dioxetane-based force-induced light emission from polymers is a powerful new way to characterize polymer behavior under stress. Here we reveal that the dioxetane is broken mechanically into products almost identical to those formed by heating at elevated temperatures (see figure). Excited- and groundstate degeneracy is thought to play a critical role in regulating the outcome of the mechanical scission process.



J. M. Clough, R. P. Sijbesma*

3565 - 3571

Dioxetane Scission Products Unchanged by Mechanical Force

F. Melin, M. R. Noor, E. Pardieu, F. Boulmedais, F. Banhart, G. Cecchini, T. Soulimane, P. Hellwig*

3572 - 3579

Investigating the Thermostability of Succinate: Quinone Oxidoreductase Enzymes by Direct Electrochemistry at SWNTs-Modified Electrodes and FTIR Spectroscopy



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Achieving thermostability: Comparative studies of the succinate: quinone reductases from mesophilic bacterium *Escherichia coli* and thermophilic bacterium *Thermus thermophilus* by using electrochemistry and infrared spectroscopy allow a discussion of the possible structural factors that contribute to the temperature-dependent activity of the studied bacteria (see figure).

P. Weerachanchai, Y. Wong, K. H. Lim, T. T. Y. Tan, J.-M. Lee*

3580 - 3591

Determination of Solubility Parameters of Ionic Liquids and Ionic Liquid/Solvent Mixtures from Intrinsic Viscosity





Viewing the Mix in 3D: The solvation power of ionic liquids and ionic liquid/ solvent mixtures was studied by using an intrinsic viscosity method that allowed the determination of Hildebrand and Hansen solubility parameters, in particular, dispersion, polar and hydrogen-bonding solubility parameters. These partial solubility parameters can be visualized as coordinates in a 3D diagram, allowing illustration of the miscibility of different materials.

E. M. Kosower,* G. Borz, I. Goldberg, N. Ermakov

3592 - 3597

N-Methyl-trimethylacetamide in Thin Films Displays Infrared Spectra of π-Helices, with Visible Static and Dynamic Growth Phases, and then a β-Sheet



Growth spurt: Increasing the size of the acyl group in a simple peptide model (*N*-methyl-acylamide) favors the formation of more open helices such as the π -helix. Sudden changes in spectroscopic data reveal that a crystalline π -helix can be formed, and a succession of further changes leads to a quasiplanar π -form. Independently, a planar β -sheet form is also obtained.

E. M. Kosower,* G. Borz

3598 - 3607

N-Alkylacylamides in Thin Films Display Infrared Spectra of 3₁₀-, α-, and π-Helices with Visible Static and Dynamic Growth Phases



Decline and fall of the Helical empire: Infrared spectroscopy of peptide

models reveals helix formation relevant to the behavior of biological molecules. Remarkable properties are demonstrated to belong to minimal peptide oligomers that are held together by hydrogen bonds alone, that is, a new species is identified in the pantheon of peptide forms.

NMRD on ultrahigh-spin coordinative clusters: The nuclear magnetic resonance relaxivities of aqueous solutions containing Fe^{III}10Dy^{III}10 ultrahigh-spin cyclic coordinative clusters have been investigated by using a wide range of

¹H Larmor frequencies up to 1.4 GHz. These single molecule magnets show interesting relaxivities and can be considered as potential relaxation agents in high-field magnetic resonance imaging.

J. R. Machado, A. Baniodeh, A. K. Powell, B. Luy, S. Krämer,* G. Guthausen*

3608 - 3613

Nuclear Magnetic Resonance Relaxivities: Investigations of Ultrahigh-Spin Lanthanide Clusters from 10 MHz to 1.4 GHz



Dyeing to quench: The solvatochromic properties of novel, effective, alkylated, aminoisocyanonaphthalene-based fluorophores are investigated. Their com-



plexation and special quenching with pyridine is studied in detail (see picture; 1: cyclohexane, 2: cyclohexane/pyridine, 3: pyridine).

M. Nagy, D. Rácz, L. Lázár, M. Purgel, T. Ditrói, M. Zsuga, S. Kéki*

3614 - 3625

Solvatochromic Study of Highly **Fluorescent Alkylated** Isocyanonaphthalenes, Their **π**-Stacking, Hydrogen-Bonding Complexation, and Quenching with Pyridine



PNDT-TTT

Thiophene length on the BHJ: An investigation of the influence of the thiophene-chain lengths of three NDT-

based polymers on the nanoscale morphologies and device performances of the active layers.

Y. J. Kim, Y. R. Cheon, J. Y. Back, Y.-H. Kim,* D. S. Chung,* C. E. Park*

3626 - 3633

Naphtho[2,1-b:3,4-b']dithiophenebased Bulk Heterojunction Solar Cells: How Molecular Structure Influences Nanoscale Morphology and **Photovoltaic Properties**

CO₂ **snaps?** The photoinduced energy transfer from poly(N-vinylcarbazole), as a donor material, to fac-(2,2'-bipyridyl)-Re(CO)₃Cl, as a catalyst acceptor, is investigated in terms of a potential application towards CO₂ reduction. Photoluminescence quenching experiments reveal dynamic quenching through resonance energy transfer in solid donor/ acceptor mixtures and in solid/liquid systems.



E. Portenkirchner,* D. Apaydin, G. Aufischer, M. Havlicek, M. White, M. C. Scharber, N. S. Sariciftci

3634 - 3638

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Photoinduced Energy Transfer from Poly(N-vinylcarbazole) to Tricarbonylchloro-(2,2'bipyridyl)rhenium(l)

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M. T. Pöschko, J. Schlagnitweit, G. Huber, M. Nausner, M. Horničáková, H. Desvaux,* N. Müller*

3639 - 3645

On the Tuning of High-Resolution NMR Probes



Out of tune: Three distinctly different tuning optima can be found for cryogenically cooled NMR probes, depending on whether pulse performance, spin noise line shape or frequency pushing are optimized. The choice of the tuning optimum has important consequences for spin dynamics.

I. Haidar, S. Lau-Truong, J. Aubard, J.-P. Renault, N. Félidj, F. Maurel, L. Boubekeur-Lecaque*

3646 - 3654

Oxadiazole-2-thiol Adsorption on Gold Nanorods: A Joint Theoretical and Experimental Study by Using SERS, XPS, and DFT



Feel the vibrations: N,S-Heterocyclic probes on gold nanorods (GNRs) and spherical gold nanoparticles (GNPs) have distinct vibrational features, as revealed by surface-enhanced Raman spectroscopy (SERS). The combination of surface analysis and density functional calculations on an Au₂₀ cluster enabled not only the identification of the coordination mode on the gold surface, but also the assignment of bands.

K. I. Lilova, C. I. Pearce, K. M. Rosso, A. Navrotsky*

3655 - 3662

Energetics of Spinels in the Fe-Ti-O System at the Nanoscale



To nano or not to nano? Assessment of the mixing thermodynamics and the effect of the particle size on Fe—Ti spinel oxides leads to an intriguing conclusion about the heats of mixing on both macro and nanoscale. The energetics of the nanosized spinel oxides turn out to be predictable based only on knowledge of their macroscale energetics and surface energies, which are consistent regardless of composition. The findings have important implications for designing nanoscale spinel oxides with desirable properties.

Heterochiral diphosphine dimers: The chirodiastaltic energy of the R_a : R_a versus R_a : S_a (PH₂-PH₂)₂ dimers amounts to 1.77 kJ mol⁻¹, which indicates that the formation of the heterochiral complex is favored.



www.chemphyschem.org

L. M. Azofra,* I. Alkorta, J. Elguero

3663 - 3670

 ΔE (hetero – homo) = –1.77 kJ mol⁻¹

Chiral Discrimination in Dimers of Diphosphines PH₂-PH₂ and PH₂-PHF

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