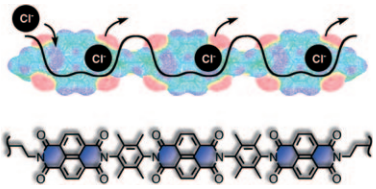
# CONCEPTS

**Transmembrane Transport**

*J. Mareda, S. Matile** ............. 28–37

**Anion–π Slides for Transmembrane Transport**



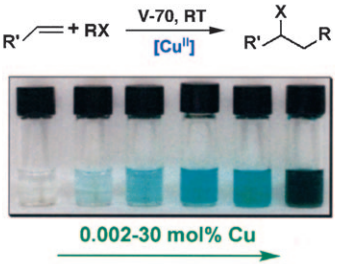
**Anion–π interactions at work, finally!** We suggest that π-acidic aromatics, such as naphthalenediimides, can be linked together to produce an unbendable scaffold with a string of binding sites for anions to move cooperatively across a lipid bilayer (see scheme).

# COMMUNICATIONS

**Atom-Transfer Radical Addition**

*T. Pintauer,* W. T. Eckenhoff, C. Ricardo, M. N. C. Balili, A. B. Biernesser, S. J. Noonan, M. J. W. Taylor* ..................... 38–41

**Highly Efficient Ambient-Temperature Copper-Catalyzed Atom-Transfer Radical Addition (ATRA) in the Presence of Free-Radical Initiator (V-70) as a Reducing Agent**

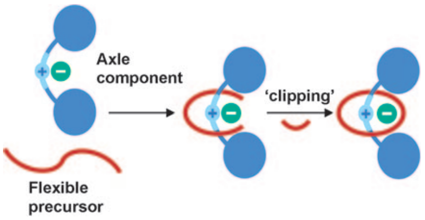


**Copper can do it!** Highly efficient ambient-temperature copper-catalyzed ATRA of polyhalogenated compounds to alkenes in the presence of free-radical initiator 2,2′-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) is reported. V-70 has shown to be a very effective reducing agent, enabling selective formation of the ATRA product with α-olefins and highly active monomers, such as methyl acrylate, methyl methacrylate, and vinyl acetate, by using as little as 0.002 mol% of copper (see figure).

**Anion Recognition**

*L. M. Hancock, P. D. Beer** ..... 42–44

**Chloride Recognition in Aqueous Media by a Rotaxane Prepared via a New Synthetic Pathway**

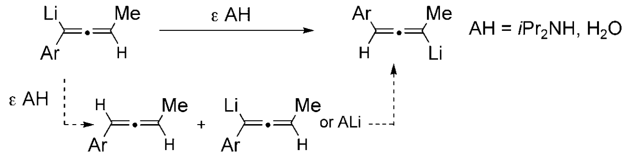


**Clip to engage a ring and interlock**: The preparation of a novel [2]rotaxane by a new synthetic pathway that exploits anion templation in combination with π–π stacking interactions is described (see scheme). Preliminary anion binding investigations reveal the rotaxane is capable of selectively recognizing chloride in aqueous solvent media in preference to basic oxoanions.

**Reaction Mechanisms**

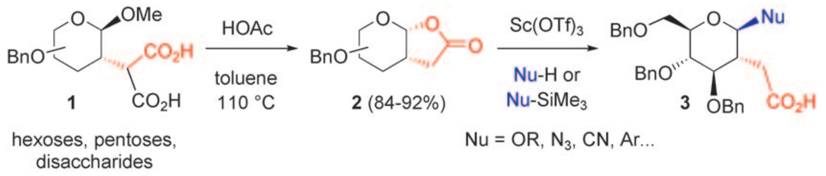
*N. Alouane, K. Bentayeb, E. Vrancken,* H. Gérard,* P. Mangeney** ..................... 45–48

**1,3-Li/H Shift of 1-Aryl-1,2-alkadienyl Reagents: An Experimental and Theoretical Study**



**A-Li shuffle**: Experimental and computational data are employed to elucidate the mechanistic aspects of the 1,3-lithium shift occurring in the allenyllithium complexes derived from 1-aryl-1-alkynes. A central role is shown to be played by proton donors, resulting in the in situ formation of a transient allene. This highlights the role of water in the reaction mechanism and explains the disconcerting non-reproducibility of "proton-free" reaction procedures.

## Carbohydrates



**Closed and re-opened for business**: C-2 branched carbohydrates **1** cyclize under conditions of decarboxylation to the hitherto unknown carbohydrate 1,2-lactones **2** in high yields. The *gluco* isomer can be opened at the anomeric position with various nuceophiles in the presence of Sc(OTf)$_3$, which allows the stereoselective synthesis of 1-functionalized glucose derivatives **3**. Thus, 1,2-*bis*-*C*-branched saccharides become available in only a few steps starting from glycals.

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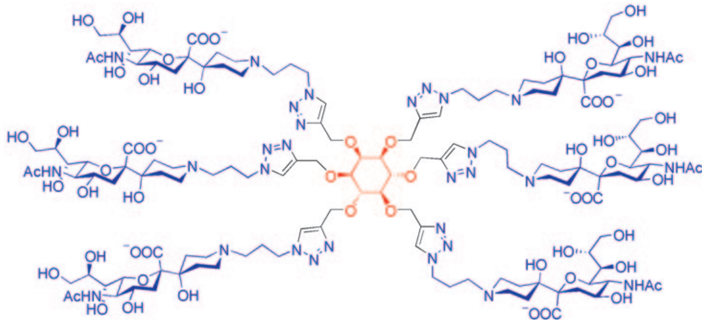
## Carbohydrate Analogues

VIP



**Diverse hydrolytically stable** carbon-linked sialoside clusters such as that depicted were prepared in good yields using a very short synthetic pathway combining, as key steps, a samarium-mediated Reformatsky coupling reaction and the copper(I)-catalyzed Huisgen azide–alkyne cycloaddition as the ligation reaction to various multifunctional scaffolds.

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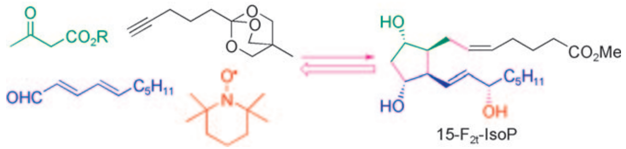
## Isoprostane Synthesis



**Cyclization/oxygenation and alkylation reactions**: A concise total synthesis of 15-F$_{2t}$-IsoP (see scheme) and its 15-epimer, today used as the gold standard marker of oxidative stress in vivo, has been accomplished in 12 steps in 14 % overall yield by applying a vinylogous aldol addition, a new oxidative radical anion cyclization/oxygenation sequence to construct the cyclopentane core, and an acetylide alkylation as the key steps.

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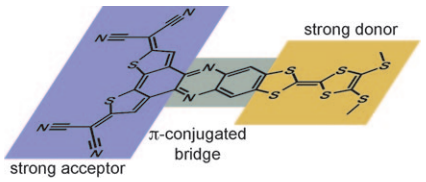
## Redox Chemistry

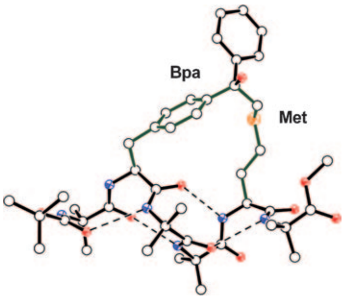
**Narrowing the gap**: A compactly fused π-conjugated molecule combines a high-lying HOMO with a low-lying LUMO ($E_{ox}-E_{red}=0.52$ eV) and a fairly low-lying LUMO+1 on the bridging unit, giving rise to strong optical charge-transfer transitions. A facile electron transfer has been observed by EPR and NMR spectroscopies.



### Helical Peptides

*A. Moretto, M. Crisma, F. Formaggio, L. A. Huck, D. Mangion, W. J. Leigh, C. Toniolo** ......................... 67–70

**Photoinduced Intramolecular Macrocyclization Reaction between a Bpa and a Met Residue in a Helical Peptide: 3D Structures of the Diastereomeric Products**

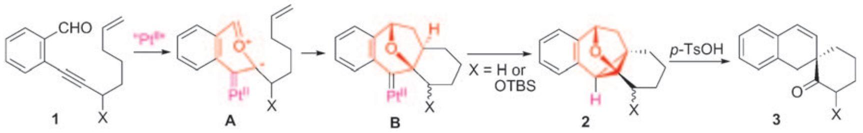


**Catch that methyl**: The first photoinduced intramolecular macrocyclization reaction in a helical peptide, containing a Bpa and a Met residue incorporated one on top of the other after a complete turn of the helix (see figure), has been performed. The photochemical remote functionalization and subsequent intramolecular cross-linking are strictly regioselective, involving exclusively the original Met side-chain ε-$CH_3$ group and generating two diastereomeric macrocyclized peptides.

### Domino Reactions

*C. H. Oh,* J. H. Lee, S. M. Lee, H. J. Yi, C. S. Hong* ............... 71–74

**Divergent Insertion Reactions of Pt–Carbenes Generated from [3+2] Cyclization of Platinum-Bound Pyrylliums**



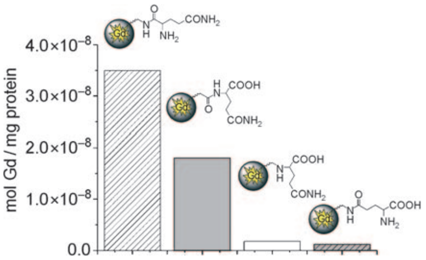
**Good fusion**: We describe the reactivity of Pt–carbene **B**, derived from enynals **1** via **A**, with Pt catalysts to afford fused cyclopropanes **2**, which are obtained by insertion into the C–H bond of the β position. Acid-catalyzed rearrangement of the cyclopropanes **2** smoothly occurred to form spiranes **3** (see scheme).

# FULL PAPERS

### Magnetic Resonance Imaging

*R. Stefania, L. Tei, A. Barge, S. Geninatti Crich, I. Szabo, C. Cabella, G. Cravotto, S. Aime** ............ 76–85

**Tuning Glutamine Binding Modes in Gd-DOTA-Based Probes for an Improved MRI Visualization of Tumor Cells**

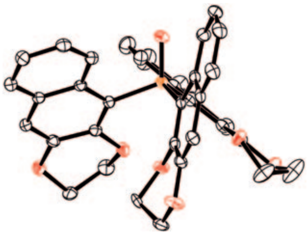


**Selective imaging**: The modulation of the binding scheme through which a glutamine residue is bound to the surface of an MR contrast agent has led to the identification of an imaging probe that is selectively taken up by hepatoma cells and not by healthy hepatocytes (see figure).

### Chirality

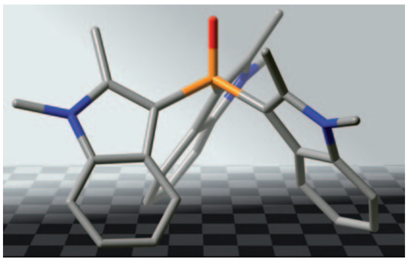
*T. Benincori, A. Marchesi, P. R. Mussini, T. Pilati, A. Ponti, S. Rizzo, F. Sannicolò** ........... 86–93

**Chirality in the Absence of Rigid Stereogenic Elements: The Absolute Configuration of Residual Enantiomers of $C_3$-Symmetric Propellers**



**Which enantiomer?** The enantiopure residual antipodes of the phosphane oxide shown here were obtained by quartz-induced crystallisation of the racemate and their absolute configuration was determined by anomalous X-ray diffraction scattering measurements. Configurational descriptors are suggested for propeller-shaped residual enantiomers.

**Three-bladed propeller-shaped molecules** may show residual stereoisomerism, a peculiar form of stereoisomerism characterized by the absence of any rigid stereogenic element (see graphic). By analyzing the relationship between configurational stability and molecular structure, directions to design configurationally stable propeller-shaped residual enantiomers have been obtained.

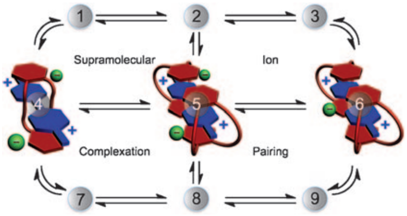


## Chirality

*T. Benincori, A. Marchesi, T. Pilati, A. Ponti,* S. Rizzo, F. Sannicolò** .................... 94–105

### Chirality in the Absence of Rigid Stereogenic Elements: The Design of Configurationally Stable $C_3$-Symmetric Propellers

**Complex ion-pairing**: Paraquat bis(hexafluorophosphate) in acetone exists as a neutral molecule and as mono- and dications, and forms at least four different host–guest complexes with dibenzo[24]crown-8 (see scheme). In this specific binding system, it is found that ion-pairing does not affect host–guest complexation.

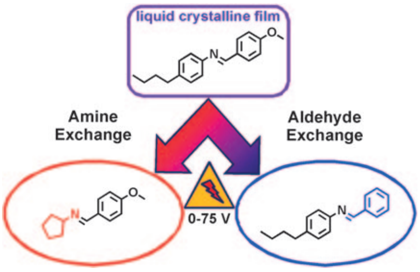


## Supramolecular Chemistry

*T. B. Gasa, J. M. Spruell, W. R. Dichtel, T. J. Sørensen, D. Philp, J. F. Stoddart,* P. Kuzmič** ...................... 106–116

### Complexation between Methyl Viologen (Paraquat) Bis(Hexafluorophosphate) and Dibenzo[24]Crown-8 Revisited

**Release with tension!** Liquid crystalline film forming imines undergo component exchange with amines and aldehydes by generating constitutional dynamic libraries. In the presence of an electric field, they expel compounds that do not participate in the formation of the liquid crystalline phase and thus allow the release of bioactive volatiles as a response to an external electric trigger (see scheme).

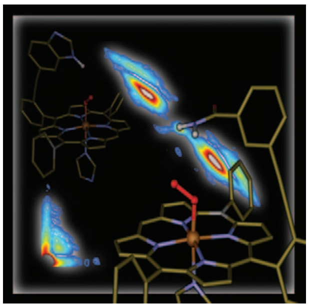


## Dynamic Combinatorial Chemistry

*A. Herrmann, N. Giuseppone, J.-M. Lehn** ..................... 117–124

### Electric-Field Triggered Controlled Release of Bioactive Volatiles from Imine-Based Liquid Crystalline Phases

**Distal hydrogen bonding** in synthetic models for hemoglobin and myoglobin are under scrutiny! Pulse EPR investigations of a series of model compounds show that simply having a hydrogen-bond donor close to bound dioxygen is not enough. A series of model compounds for dioxygen binding heme proteins (see figure, for example) is investigated in terms of their distal hydrogen-bonding properties by pulse EPR spectroscopy. The structural requirements for this interaction to take place are elaborated.



## Molecular Recognition

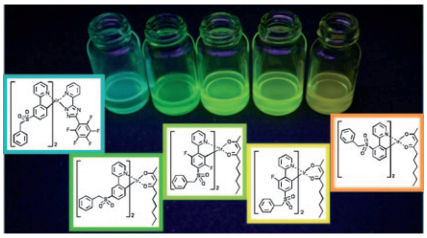
*H. Dube, B. Kasumaj, C. Calle, B. Felber, M. Saito, G. Jeschke,* F. Diederich** ................... 125–135

### Probing Hydrogen Bonding to Bound Dioxygen in Synthetic Models for Heme Proteins: The Importance of Precise Geometry

## Luminescence

*R. Ragni, E. Orselli, G. S. Kottas, O. H. Omar, F. Babudri, A. Pedone, F. Naso, G. M. Farinola,* L. De Cola** ..................... 136–148

**Iridium(III) Complexes with Sulfonyl and Fluorine Substituents: Synthesis, Stereochemistry and Effect of Functionalisation on their Photophysical Properties**

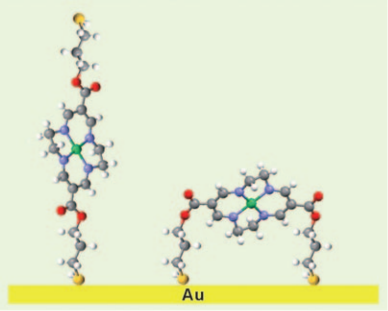


**Reaching for the rainbow**: A sulfonyl moiety has been introduced as a functional group in phenylpyridine ligands of heteroleptic iridium complexes. The sulfonyl substituent enables the tuning of emission in a wide range of colours (see graphic).

## Self-Assembled Monolayers

*U. E. Wawrzyniak, M. Woźny, J. Kowalski, S. Domagała, E. Maicka, R. Bilewicz,* K. Woźniak,* B. Korybut-Daszkiewicz** ..... 149–157

**Neutral Nickel(II) and Copper(II) Tetraazamacrocyclic Complexes as Molecular Rods Attached to Gold Electrodes**

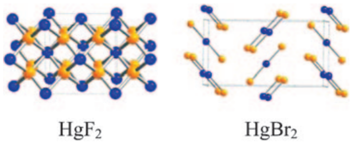


**A potential switch?** New derivatives of neutral macrocyclic complexes functionalized with 3-mercaptopropyl groups self-assemble into well-organized, single-component, and mixed monolayers on gold electrodes (see figure). The macrocyclic donor sites interact with the cyclic acceptor cations in the solution, leading to the formation of pseudorotaxane structures on the electrode surface. These interactions are switched off upon application of appropriate potential at which the surface-immobilized complex is oxidized.

## Structural Chemistry

*K. J. Donald,* M. Hargittai,* R. Hoffmann** ................... 158–177

**Group 12 Dihalides: Structural Predilections from Gases to Solids**

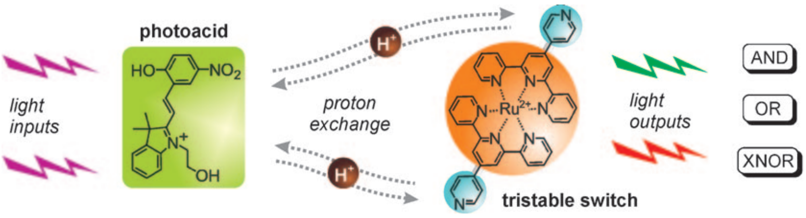


**Interplay of ionic and covalent factors**: Connections between the structures of Group 12 dihalides in their vapor and crystal phases are sought and discussed. The exceptional rigidity of $HgX_2$ monomers, the preference for a loosely bound $C_{2h}$ $HgX_2$ dimer structure, relative to a $D_{2h}$ structure for the Zn and Cd analogues, and the diversity of structure types in the $HgX_2$ solids (see picture) are linked through the interplay of ionic and covalent factors constrained by relativistic and shell structure effects.

## Molecular Devices

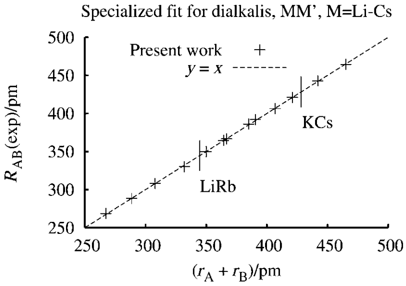
*S. Silvi, E. C. Constable, C. E. Housecroft, J. E. Beves, E. L. Dunphy, M. Tomasulo, F. M. Raymo,* A. Credi** ...... 178–185

**All-Optical Integrated Logic Operations Based on Chemical Communication between Molecular Switches**



**Light logic**: A chemical system based on the coupled operation of an acid–base-switchable ruthenium complex and a photochromic compound in solution (see scheme) can execute logic functions with both in- and output optical signals.

**Bond—Single Bond!** A new set of single-bond covalent radii for $Z=1$–118 is obtained from a self-consistent fit. Its mean-square deviation, $\delta$, is under 3 pm. For specialized sets, like those shown here, $\delta$ can be lowered below 1 pm.



## Computational Chemistry

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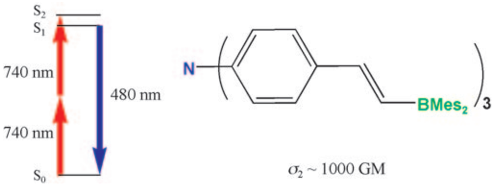

**Superior two-photon absorption response**: Conjugated dipolar, pseudo-quadrupolar (V-shaped) and octupolar (trigonal) molecular systems containing nitrogen-donor and boron-acceptor moieties have been synthesised. The octupolar compound tris($E$-4-dimesitylborylethenylphenyl)amine has been shown to exhibit a large two-photon absorption cross-section of approximately 1000 GM at 740 nm (see figure).

## Luminescence

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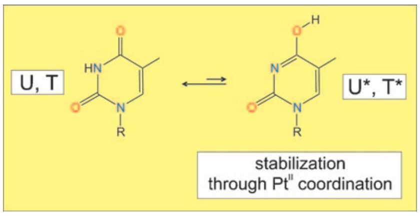
**Relative stabilities of tautomers** of uracil and thymine nucleobases can be strongly perturbed by $Pt^{II}$ coordination, up to the extent that a Pt-complexed rare keto, hydroxo tautomer approaches or even surpasses the Pt-complexed major diketo tautomer in stability (see scheme). DFT calculations reveal the importance of co-ligands, overall charge of the complex, and the role of water.



## Bioinorganic Chemistry

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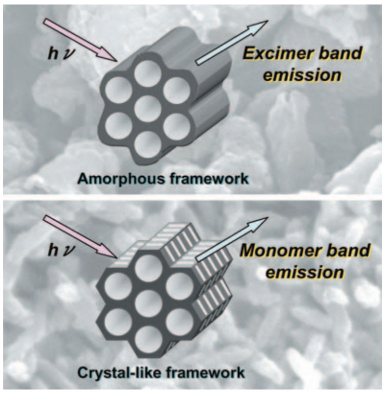
**A true reflection**: Unique fluorescence behavior that reflects molecular-scale ordering of frameworks is observed for 2,6-naphthylene-bridged mesoporous organosilicas. This key finding suggests a potential to control the interactions between organic groups and thus the optical properties of inorganic/organic hybrids (see picture).

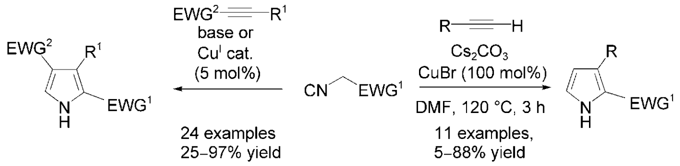


## Hybrid Materials

## Pyrrole Synthesis

*A. V. Lygin, O. V. Larionov, V. S. Korotkov, A. de Meijere** ................... 227 – 236

### Oligosubstituted Pyrroles Directly from Substituted Methyl Isocyanides and Acetylenes



**Convenient pyrrole syntheses**: Two new protocols have been developed for one-pot, one-step formal [3+2] cycloadditions of substituted methyl isocyanides onto the triple bond of either acceptor-activated internal or non-activated terminal acetylenes leading to 2,3,4-trisubstituted and 2,3-disubstituted pyrroles, respectively (see scheme).

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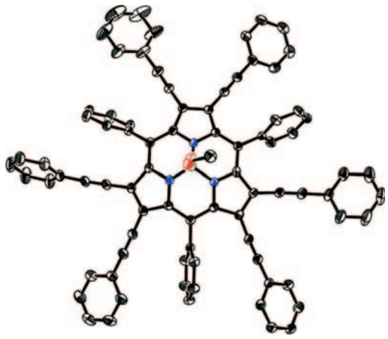
## Porphyrinoids

*E. Tsurumaki, Y. Inokuma, S. Easwaramoorthi, J. M. Lim, D. Kim,* A. Osuka** ........... 237 – 247

### Peripheral Hexabromination, Hexaphenylation, and Hexaethynylation of *meso*-Aryl-Substituted Subporphyrins



**β-Substituted subporphyrins**: β-Hexabrominated, hexaphenylated, and hexaethynylated (see picture) *meso*-aryl subporphyrins are reported as the first products of β-peripherally fabricated subporphyrins. X-ray diffraction analysis revealed that all hexasubstituted subporphyrins preserve bowl-shaped structures. Detailed NMR, electrochemical, optical, and theoretical studies were carried out.

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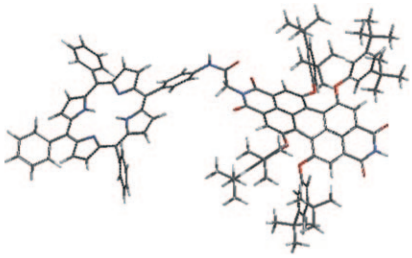
## Porphyrin Dyads

*S. Mathew, M. R. Johnston** . . 248 – 253

### The Synthesis and Characterisation of a Free-Base Porphyrin–Perylene Dyad that Exhibits Electronic Coupling in Both the Ground and Excited States



**Sharing more than a covalent bridge!** A free-base porphyrin–perylene dyad (shown here) possessing a unique methylene amide bridge was synthesised in a divergent manner. Characterisation by absorption spectroscopy showed the presence of electronic coupling, which was further probed through steady-state fluorometric studies.

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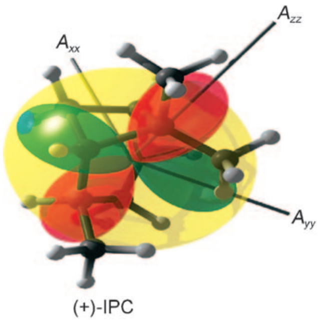
## Enantiodiscrimination

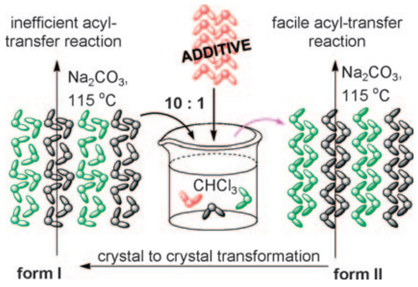
*A. Marx, C. M. Thiele** ........ 254 – 260

### Orientational Properties of Poly-γ-benzyl-L-glutamate: Influence of Molecular Weight and Solvent on Order Parameters of the Solute



**All lined up!** Modulating the order induced by alignment media is of prime importance when measuring residual dipolar couplings (RDCs). By using PBLGs of different molecular weights, the degree of order induced can be adjusted, leading to well-resolved spectra. The orientation of the solute (with respect to $B_0$) and the enantiodiscriminating properties of the liquid crystal, however, are not changed (see figure).

**A pinch of an additive**: Additives have a profound influence on molecular organization in crystals, which accounts for their physical and chemical properties. We describe how a rationally chosen structurally similar enantiomeric additive could be used to produce metastable crystals of racemic 2,4-di-*O*-benzoyl-*myo*-inositol-1,3,5-orthoacetate that exhibit neat intermolecular acyl-transfer reactivity (see scheme).



## Solid-State Reactions

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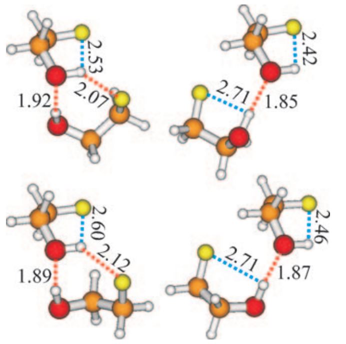
**Competitive formation of intra- and intermolecular hydrogen bonds**: Molecular self-recognition in the dimeric 2-fluoroethanol conformers has been studied by using high resolution rotational spectroscopy and ab initio methods. Four conformers (see graphic) with compact geometries were detected experimentally. The effects of fluorination and the competing inter- and intramolecular hydrogen bonds on the stability of the conformers have been investigated.



## Rotational Spectroscopy

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* Author to whom correspondence should be addressed

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