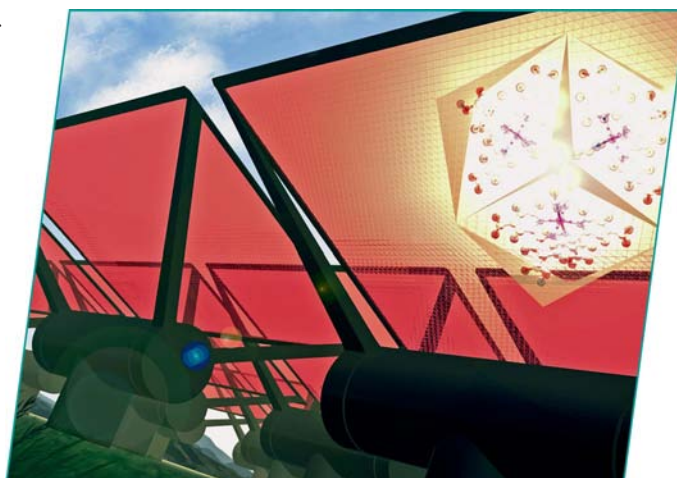


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## COVER PICTURE

The cover picture shows the molecular structure of three ruthenium polypyridyl complexes, namely the tris(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)–2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid tris(tetrabutylammonium) salt (commonly known as Black Dye). The background of the picture corresponds to the drawing of a series of dye-sensitised solar cells, which use ruthenium complexes as photosensitisers. This is the topic of the Microreview by A. Reynal and E. Palomares on p. 4509ff, in which the properties, synthetic routes and main applications of the most relevant ruthenium–polypyridyl complexes are presented in further detail.



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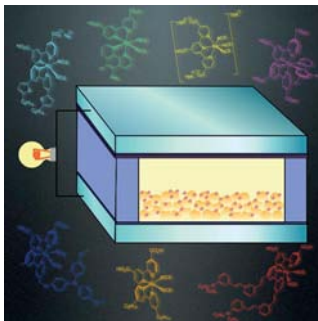
## MICROREVIEW

### Dye Solar Cells

A. Reynal,\* E. Palomares\* ..... 4509–4526

Ruthenium Polypyridyl Sensitisers in Dye Solar Cells Based on Mesoporous  $\text{TiO}_2$

**Keywords:** Dye-sensitized solar cells / Ruthenium / Charge transfer / Sensitizers



The review describes dye solar cells and the use of ruthenium complexes as sensitizers in this molecular device.

## FULL PAPERS

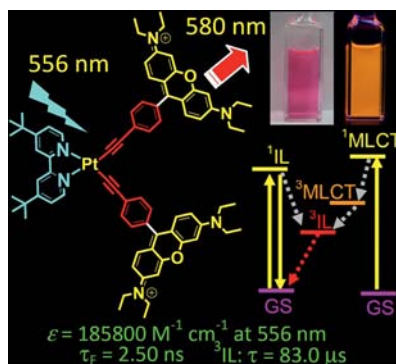
### Photochemistry

L. Huang, L. Z., H. Guo, W. Wu, W. Wu, S. Ji, J. Zhao\* ..... 4527–4533



Room-Temperature Long-Lived  $^3\text{IL}$  Excited State of Rhodamine in an  $N^{\wedge}N$   $\text{Pt}^{\text{II}}$  Bis(acetylide) Complex with Intense Visible-Light Absorption

**Keywords:** Photochemistry / Rhodamine / Platinum / Triplet–triplet annihilation / Upconversion / Chromophores



An  $N^{\wedge}N$   $\text{Pt}^{\text{II}}$  bis(acetylide) complex containing rhodamine was prepared ( $\text{Pt-Rho}$ ), which shows intense UV/Vis absorption at 556 nm ( $\epsilon = 185800 \text{ M}^{-1} \text{ cm}^{-1}$ ), fluorescence of the ligand, and prolonged triplet excited state lifetime ( $\tau_{\text{T}} = 83.0 \mu\text{s}$ , rhodamine-localised  $^3\text{IL}$  state).  $\text{Pt-Rho}$  was used as sensitizer for triplet–triplet annihilation upconversion, and an upconversion quantum yield of 11.2% was observed.

### Bimetallic Nanoparticles

M. A. Uppal, M. B. Ewing, I. P. Parkin\* ..... 4534–4544

One-Pot Synthesis of Core-Shell Silver-Gold Nanoparticle Solutions and Their Interaction with Methylene Blue Dye

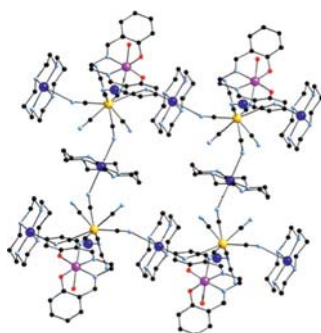
**Keywords:** Nanoparticles / Colloids / Silver / Gold / Dyes / Metal–Dye interactions



The one-pot synthesis of a range of silver-gold core-shell colloids is presented. These core-shell particles were characterised by several methods and shown to consist primarily of silver cores and gold exteriors that were slightly oxidised at the surface by the surfactant. The effect of methylene blue

dye absorption onto these colloids was monitored. An increase in the extinction coefficient of the dye was observed. The different levels of increase in the extinction coefficient for the silver-gold colloids versus the pure metal colloids were explained.

By using the stepwise “polynuclear complex as ligand” synthetic approach, we succeeded in obtaining an original cyano-based heterotrimetallic bidimensional network:  $[\text{Mo}(\text{CN})_8\{\text{Cu}(\text{cyclam})\}_2\text{Mn}(\text{salen})\cdot(\text{H}_2\text{O})](\text{ClO}_4)$  [cyclam = 1,4,8,11-tetraazacyclotetradecane,  $\text{H}_2\text{salen}$  = 1,2-bis(salicylideneamino)ethane] based on molybdenum(IV), copper(II), and manganese(III). We report its synthesis, X-ray structure, and magnetic properties.



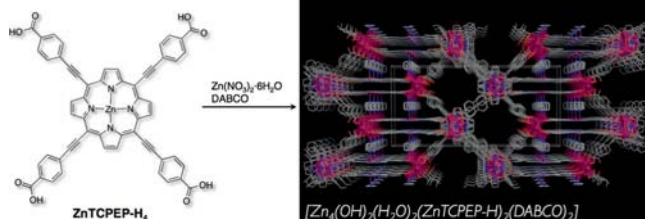
Bidimensional  $\text{Mo}^{\text{IV}}\text{Cu}^{\text{II}}$  square-sheet network with pendant  $\text{Mn}^{\text{III}}$

**J. Long, L.-M. Chamoreau,  
V. Marvaud\*** ..... 4545–4549

Supramolecular Heterotrimetallic Assembly Based on Octacyanomolybdate, Manganese, and Copper

**Keywords:** Cyanides / Copper / Manganese / Molybdenum / Magnetic properties / Supramolecular chemistry

## Porphyrin-Based Porous MOFs



We have designed a new tetracarboxylporphyrin building block,  $\text{ZnTCPEP-H}_4$ , and used it in the construction of a novel porphyrin-based metal carboxylate framework,  $\text{Zn}_4\cdot\text{ZnTCPEP}\cdot\text{DABCO}$ , which has

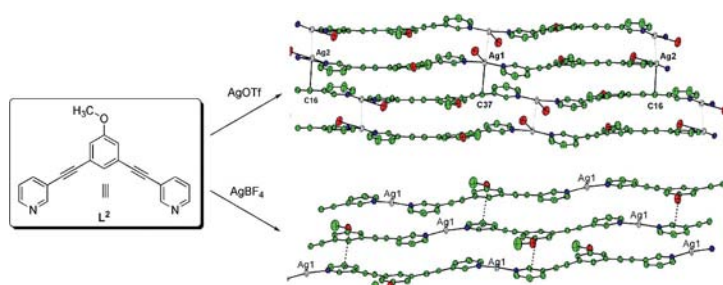
a 3D network topology.  $\text{Zn}_4\cdot\text{ZnTCPEP}\cdot\text{DABCO}$  has a BET surface area of  $461\text{ m}^2/\text{g}$ , a Langmuir surface area of  $581\text{ m}^2/\text{g}$ , and a hydrogen adsorption capacity of  $0.86\text{ wt.}\%$  at  $77\text{ K}$  and  $0.1\text{ MPa}$ .

**S. Matsunaga,\* N. Endo,  
W. Mori\*** ..... 4550–4557

A New Metal Carboxylate Framework Based on Porphyrin with Extended  $\pi$ -Conjugation

**Keywords:** Microporous materials / Zinc / Metal–organic frameworks / Porphyrins / Carboxylate ligands

## Silver(I) Coordination Polymers



A family of silver(I) coordination polymers  $[\text{AgL}^2\text{X}]_n$  (**1**) has been prepared and characterized from silver salts  $\text{AgX}$  ( $\text{X} = \text{CF}_3\text{SO}_3, \text{BF}_4, \text{NO}_3, \text{PF}_6$ ) and 5-methoxy-1,3-bis(pyridin-3-ylethynyl)benzene ( $\text{L}^2$ )

acting as a bidentate ligand.  $[\text{AgL}^2\text{CF}_3\text{SO}_3]_n$  (**1a**) and  $[\{\text{AgL}^2\}\{\text{BF}_4\}]_n$  (**1b**) were structurally characterized. The influence of the anions and intermolecular aromatic interactions on the packing are reported.

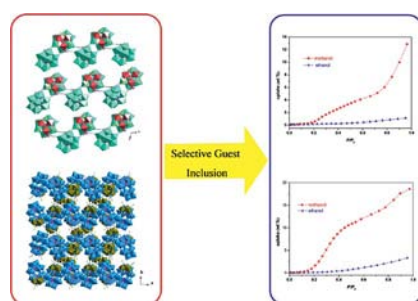
**C. Desmarets,\* I. Azcarate, G. Gontard,  
H. Amouri\*** ..... 4558–4563

A Rigid Angular Bidentate Ligand for the Design of a New Class of Coordination Polymers Based on Silver(I) Salts – Influence of the Anion on Coordination Assemblies

**Keywords:** Coordination chemistry / Coordination polymers / Silver / Ligand design / Self-assembly

## Nanoporous Ionic Crystals

Based on polyoxometalate anions and macrocations,  $\text{KH}_2[\text{Cr}_3\text{O}(\text{OOCCH}_3)_6\cdot(\text{H}_2\text{O})_3][\alpha\text{-GeMo}_{12}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$  (**1**),  $\text{K}_{1.5}\text{H}_{1.5}[\text{Cr}_3\text{O}(\text{OOCCH}_3)_6\cdot(\text{H}_2\text{O})_3][\alpha\text{-GeW}_{12}\text{O}_{40}]\cdot 9.5\text{H}_2\text{O}$  (**2**),  $\text{NaH}_2[\text{Cr}_3\text{O}(\text{OOCCH}_3)_6\cdot(\text{H}_2\text{O})_3][\alpha\text{-P}_2\text{W}_{18}\text{O}_{62}]\cdot 32\text{H}_2\text{O}$  (**3**), and  $\text{Na}_3[\text{Cr}_3\text{O}(\text{OOCCH}_3)_6\cdot(\text{H}_2\text{O})_3][\alpha\text{-As}_2\text{W}_{18}\text{O}_{62}]\cdot 34\text{H}_2\text{O}$  (**4**) have been prepared and characterized.



**X. Han, L. Xu,\* F. Li,  
N. Jiang** ..... 4564–4570

A New Series of Nanoporous Ionic Crystals Based on Polyoxometalates – Synthesis, Crystal Structures, and Adsorption Properties

**Keywords:** Polyoxometalates / Adsorption / Microporous materials / Ionic crystals / Channel structures

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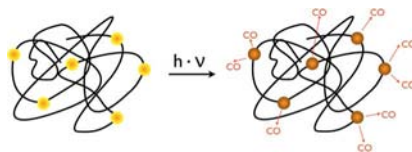
## CO-Releasing Molecules

N. E. Brückmann, M. Wahl,  
G. J. Reiß, M. Kohns, W. Wätjen,  
P. C. Kunz\* ..... 4571–4577



Polymer Conjugates of Photoinducible  
CO-Releasing Molecules

**Keywords:** Carbon monoxide / Carbonyl  
ligands / Polymer conjugates / Manganese /  
EPR effect / Cytotoxicity



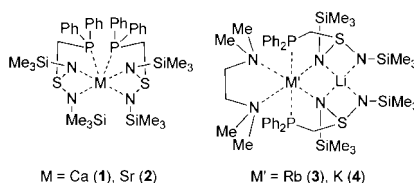
Functionalised copolymers of 2-hydroxypropyl methacrylate and acrylamide (HPMA) were designed as polymeric carrier systems to deliver organometallic drugs, for example,  $\text{Mn}(\text{CO})_3$  photo-CORMs, to tumour tissue and centres of inflammation.

## Ligand Design

M. M. Meinholz,  
D. Stalke\* ..... 4578–4584

Monoanionic N,P,S-Janus Head Tripods in  
s-Block Metal Coordination

**Keywords:** Sulfur / Ligand design / N,P,S  
ligands / s-Block metals / Solid-state structures



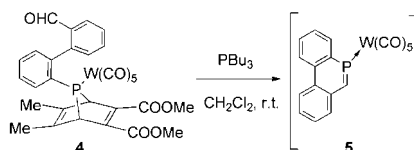
$[(\text{tmeda})\text{Li}\{\text{Ph}_2\text{PCH}_2\text{S}(\text{NSiMe}_3)_2\}]$  contains a *N*-chelated lithium cation that is easy to replace with other s-block metals. The phosphanyl side arm of the ligand provides a coordination site that is softer than the N atoms and allows for the synthesis of heterobimetallic complexes; while the P atom contributes to the tripodal facial coordination with Ca (1) and Sr (2) and binds with the secondary metals Rb (3) and K (4). In complexes 3 and 4 lithium is the structural anchor.

## Phosphanines

H. Wang, W. Zhao, Y. Zhou, Z. Duan,\*  
F. Mathey\* ..... 4585–4589

A Phospha-Wittig Route to 5-Phospha-  
phenanthrene

**Keywords:** Cycloaddition / Phosphorus  
heterocycles / Phospha-Wittig reaction



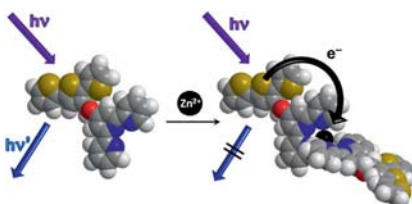
The reaction of 4 with tributylphosphane at room temperature gives phosphaphenanthrene complex 5, which can be detected by  $^{31}\text{P}$  NMR and trapped by addition, and [2+4] or [2+3] cycloaddition.

## Terthiophene Systems

G. Bergamini, L. Boselli, P. Ceroni,\*  
P. Manca, G. Sanna, M. Pilo\* ... 4590–4595

Terthiophene Appended with Terpyridine  
Units as Receptors for Protons and  $\text{Zn}^{2+}$   
Ions: Photoinduced Energy and Electron  
Transfer Processes

**Keywords:** Zinc(II) complexes / Luminescence / Oligothiophenes / Electrochemistry



Coupling of terthiophene and terpyridine units leads to luminescent and electroactive systems with potential applications as sensors of protons and metal ions.

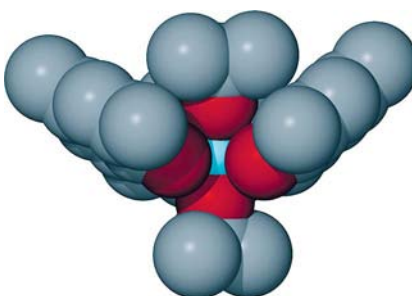
## Polymerisation

S. L. Hancock, M. F. Mahon,  
G. Kociok-Köhn, M. D. Jones\* ... 4596–4602



Homopiperazine and Piperazine Com-  
plexes of  $\text{Zr}^{\text{IV}}$  and  $\text{Hf}^{\text{IV}}$  and Their Appli-  
cation to the Ring-Opening Polymerisation  
of Lactide

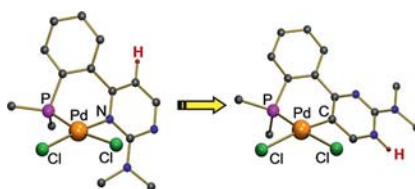
**Keywords:** Titanium / Zirconium / Haf-  
nium / Ring-opening polymerization / Sus-  
tainable chemistry



New group 4 bis(phenolate) complexes have been prepared and characterised in the solid state. The complexes have been tested for the ring-opening polymerization (ROP) of *rac*-lactide both in the melt and solution with low polydispersity indices. In the solid state, the isopropoxide complexes adopt a *trans* configuration.



NH<sub>2</sub> versus NR<sub>2</sub>: Subtle steric requirements determine the reactivity of palladium complexes bearing aminopyrimidinyl phosphane ligands and their performance as catalysts in Suzuki–Miyaura coupling reactions.

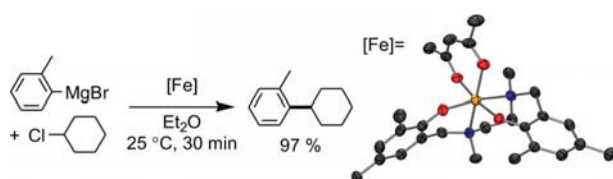


S. Farsadpour, L. T. Ghoochany, Y. Sun,  
W. R. Thiel\* ..... 4603–4609

Small Substituents Make Large Differences: Aminopyrimidinyl Phosphanes Undergoing C–H Activation

**Keywords:** P,N ligands / C–H activation / Palladium / Phosphanes

## Iron(III) Phenolato Complexes



Iron(III)acac complexes supported by tetradentate N,O ligands have been prepared and structurally characterized. Their attempted use as single component, air-

stable catalysts for C–C cross coupling of aryl Grignard reagents with secondary alkyl bromides and chlorides is presented.

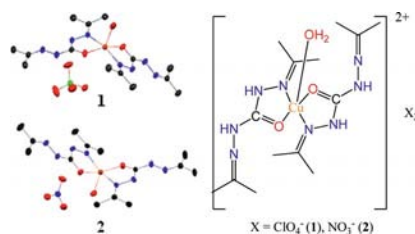
K. Hasan, L. N. Dawe,  
C. M. Kozak\* ..... 4610–4621

Synthesis, Structure, and C–C Cross-Coupling Activity of (Amine)bis(phenolato)-iron(acac) Complexes

**Keywords:** Transition metals / Iron / N,O ligands / Cross-coupling / Homogeneous catalysis

## Organometallic Energetic Materials

Crystal structures of copper(II) complexes with carbohydrazone derivatives prove the five-membered ring coordination mode of copper with carbohydrazone. Synthesized compounds exhibit properties of pyrotechnic flame colorants generating blue and green colors.



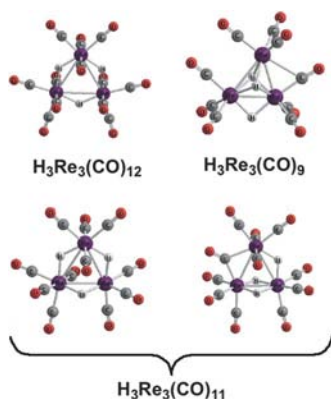
O. S. Bushuyev, F. A. Arguelles,  
P. Brown, B. L. Weeks,  
L. J. Hope-Weeks\* ..... 4622–4625

New Energetic Complexes of Copper(II) and the Acetone Carbohydrazone Schiff Base as Potential Flame Colorants for Pyrotechnic Mixtures

**Keywords:** Copper / Flame colorants / Calorimetry

## Bridging Hydrogen Atoms

The lowest energy H<sub>3</sub>Re<sub>3</sub>(CO)<sub>12</sub> and H<sub>3</sub>Re<sub>3</sub>(CO)<sub>11</sub> structures have central Re<sub>3</sub> triangles with edge-bridging hydrogen atoms. The Re<sub>3</sub> triangles in the lowest energy H<sub>3</sub>Re<sub>3</sub>(CO)<sub>10</sub> and H<sub>3</sub>Re<sub>3</sub>(CO)<sub>9</sub> structures have one and two face-bridging hydrogen atoms, respectively, with the remaining hydrogen atoms in edge-bridging positions.



N. Li,\* Y. Xie, R. B. King,\*  
H. F. Schaefer III ..... 4626–4636

Edge-Bridging and Face-Bridging Hydrogen Atoms in Trinuclear Rhenium Carbonyl Hydrides

**Keywords:** Rhenium / Bridging ligands / Density functional calculations / Thermochemistry

\* Author to whom correspondence should be addressed.

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