Click chemistry: the emerging role of the azide-alkyne Huisgen dipolar addition in the preparation of substituted tetrapyrrolic derivatives

Fabienne Dumoulin* and Vefa Ahsen*

A summary of the use of Huisgen azide-alkyne dipolar addition in the synthesis of tetrapyrrolic compounds, mainly porphyrins, phthalocyanines, chlorins and bacteriochlorins is given in this review.

Encoding isotopic watermarks in molecular electronic materials as an anti-counterfeiting strategy. Application to porphyrins for information storage

Jonathan S. Lindsey*, Patchanita Thamyongkit, Masahiko Taniguchi and David F. Bocian*

The provenance of tetrapyrrole macrocycles employed in molecular electronics applications can be ensured by isotopic substitution — achieved by rational and/or combinatorial procedures — integral to the macrocycle. A mixture of macrocycles with various isotopic composition (isotopically unmodified, isotopologues, isotopomers) provides the molecular equivalent of an indelible printed watermark. Resonance Raman spectroscopic examination can reveal the watermark, but not the underlying molecular and isotopic composition; imaging mass spectrometry can reveal the presence of isotopologues but cannot discriminate among isotopomers.
Articles

pp. 534–538
Synthesis of a diimidazolylporphyrin pincer palladium complex
Jun Yamamoto, Tomohiro Shimizu, Shigeru Yamaguchi, Naoki Aratani, Hiroshi Shinokubo* and Atsuhiro Osuka*

A porphyrin pincer palladium complex in which the palladium atom is supported by two imidazolyl groups has been synthesized and characterized by spectroscopic and the X-ray diffraction analysis. The catalytic activity of the complex has been investigated in the Mizoroki-Heck reaction of iodobenzene with butyl acrylate.

pp. 539–546
Crown ether functionalized texaphyrin monomers and dimers
Christian Preihs, Darren Magda and Jonathan L. Sessler*

The first 18-crown-6 functionalized texaphyrin derivatives are reported. Both crown ether functionalized species proved to be stable at physiological pH and revealed distinct shifts in the UV spectrum when treated with sodium-, potassium-, ammonium- or zinc(II)-salts. Their in vitro anticancer activity was tested in in vitro cell activity studies.

pp. 547–554
Preparation and electrochemical and optical properties of α-octaalkylphthalocyanines with four fused TTF units
Takeshi Kimura*, Toshiharu Namao, Kaori Amano, Nobuhiro Takahashi, Yutaka Takaguchi, Tomonori Hoshi and Nagao Kobayashi*

α-Octaalkyltettrakis(tetraethylfulvaleno)phthalocyanines were prepared by treatment of 3,6-dialkylphthalonitriles with lithium in 1-hexanol, respectively. Electrochemical and optical properties of α-octaalkyltettrakis(tetraethylfulvaleno)phthalocyanines were examined by cyclic voltammetry and UV-vis and MCD spectroscopy.

pp. 555–559
One-step synthesis of α/β cyano-aqua cobinamides from vitamin B12 with Zn(II) or Cu(II) salts in methanol
Kai Zhou and Felix Zelder*

This short communication describes the screening of various metal salts for the preparation of cyano-aqua cobinamides from vitamin B12 in methanol. ZnCl₂ and Cu(NO₃)₂·3H₂O have been identified as most active for this purpose and represent useful alternatives to the widely applied Ce(III) method that requires excess cyanide.

pp. 560–574
Room temperature ionic liquids based on cationic porphyrin derivatives and tetrakis(pentafluorophenyl)borate anion
Hai-Jun Xu, Claude P. Gros, Stéphane Brandès, Pei-Yu Ge, Hubert H. Girault and Jean-Michel Barbe*

A series of 11 low melting ionic liquids based on meso-substituted A₂B₂-porphyrins and A₂B₄-porphyrins containing one or two pyridyl substituents were synthesized in high yields. Three of them are liquids at room temperature. The thermal properties and conductivity values of these salt derivatives were also measured. A specific conductivity value of up to 4 mS/cm⁻¹ was obtained for a compound having the counter-anion B(C₆F₅)₄⁻.

pp. 575–582
A new approach to N-phenylquinolino[2,3,4-at]porphyrins. Electrochemical and photochemical studies
Ana M.V.M. Pereira, Maria G.P.M.S. Neves, José A.S. Cavaleiro*, Jean-Paul Gisselbrecht, Christophe Jeandon and Romain Ruppert* 

A new route to N-phenylquinolino[2,3,4-at]porphyrins is described and the electrochemical and photochemical properties of the synthesized derivatives were investigated. The electrochemical studies (cyclic voltammetry and rotating disk voltammetry) of the free base and the corresponding Ni, Cu and Pd complexes have shown that the presence of the phenyl group is responsible for the formation of stable radical cations.

pp. 583–591
Solvent-dependent rotational phenomena in μ-nitrado[2,3,9,10,16,17,23,24-octa(n-pentoxy)phthalocyaninato]diiron complex
Evgeny V. Kudrik, Pavel Afanasiev, Denis Bouchu and Alexander B. Sorokin*

UV-vis, ¹H NMR and XANES data reveal the presence of two different forms in apolar and polar solvents. The difference in properties between the two forms is explained by solvent-dependent mutual orientation of two phthalocyanine rings. Tuning of the structure of N-bridged diiron macrocyclic complexes by introduction of substituents and modification of electronic properties of the complexes via conformation changes might be useful for optimization of their catalytic and material properties.
CONTENTS

pp. 592–597
Influencing parameters for the achievement of porphyrin supramolecular architectures on mesoporous metal oxide nanoparticles
Miquel Planells, Almudena González, Pablo Ballester* and Emilio Palomares*

Spectroscopic characterization of a supramolecular trisporphyrin complex that is heterogeneously self-assembled onto mesoporous Al₂O₃ films is described. The parameters for an efficient complexation process, such as dye loading, were evaluated and discussed.

pp. 598–601
Structural investigations of hexadecafluoro(phthalocyaninato)ruthenium(II) F₁₆PcRu with EXAFS spectroscopy
Helmut Bertagnolli*, Venkata Krishnan, Tamer Ezzat Youssef and Michael Hanack*

Amorphous hexadecafluoro(phthalocyaninato)ruthenium(II) F₁₆PcRu has been studied with EXAFS spectroscopy. It is shown that F₁₆PcRu has a dimeric structure in the solid state.

pp. 602–611
Synthesis of chiral ruthenium and cobalt (meso-2-amidophenyl)porphyrins and their catalytic activity in cyclopropanation reactions
Nicolas Raoul, Emma Gallo* and Eric Rose*

Preparation of chiral porphyrin ligands and of their ruthenium and cobalt complexes is reported. These complexes have been used as catalysts in cyclopropanation and amination reactions.

pp. 612–621
Synthesis, characterization, X-ray structure, and mixed-valence states of trans-dichlorotin(IV)-5,10,15,20-tetraferrocenylporphyrin
Pavlo V. Solntsev, Ben D. Neisen, Jared R. Sabin, Nikolay N. Gerasimchuk and Victor N. Nemykin*

A new trans-dichlorotin(IV)-5,10,15,20-tetraferrocenylporphyrin was prepared and characterized by spectroscopic (NMR, UV-vis, MCD, and APCI MS), electrochemical (CV and DPV), spectroelectrochemical, and chemical oxidation approaches. Single crystal X-ray analysis reveals unusual α,α',β,β'-conformation of the ferrocenyI substitutents in a solid state. Conformational analysis and electronic structures of the individual atropisomers were investigated using DFT approach.
pp. 622–631  
Synthesis, structure and spectroscopic properties of a porphycene-Re¹ complex  
Weina Zhang, Yi Chang, Fan Wu, John Mack, Nagao Kobayashi* and Zhen Shen*  
A new type of rhenium(I) tricarbonyl porphycene complex was prepared and its structure solved by single-crystal X-ray work. Its spectral and electrochemical properties are described. Molecular orbital calculations were also performed to analyze the electronic structure of this compound.

pp. 632–638  
Development of the synthesis of the diamine complexes of covalent conjugates of platinum(II) with octacarboxy-substituted cobalt phthalocyanine  
Olga Dolotova* and Oleg L. Kaliya  
Ethylendiamine-N,N’-diacetic acid complexes of the covalent conjugates of octacarboxy-substituted cobalt phthalocyanine with one, two and three platinum atoms were synthesized and characterized by elemental analysis, electronic absorption, IR and mass spectra data.

pp. 639–651  
Porphyrin hexamer with a triphenylene core unit. Spectroscopy, electrochemistry and controllable supramolecular formation  
Hayato Sakai, Mohammad Gulam Rabbani and Taku Hasobe*  
A series of free-base and zinc porphyrin hexamers, where six porphyrin units are linked to a triphenylene core through amide or ester linkage, was designed and synthesized. The spectroscopic and electrochemical properties, as well as supramolecular formations of porphyrin hexamers are discussed in detail.

pp. 652–658  
Vilsmeier-Haack formylation of Cu(II) and Ni(II) porphyrin complexes under microwaves irradiation  
Nuno M.M. Moura, Maria A.F. Faustino*, Maria G.P.M.S. Neves*, Armando C. Duarte and José A.S. Cavaleiro  
An improvement in the Vilsmeier-Haack formylation of Ni(I) and Cu(II) complexes of meso-tetraarylporphyrins by using microwave irradiation is reported. Formyl derivatives were isolated in better yields when compared with the ones obtained under classical heating conditions and with a significant reduction on the reaction times. Scaled-up studies show that the efficiency of the process is not affected by increasing the amount of porphyrin.

pp. 659–666
Synthesis and characterization of high molecular weight phthalocyanine-PPV copolymers through post-polymerization functionalization
Juan-José Cid, Jan Duchateau, Ineke Van Severen, Carolina R. Ganivet, Gema de la Torre, Purificación Vázquez, Thomas Cleij, Laurence Lutsen, Dirk Vanderzande* and Tomás Torres*

High molecular weight poly(p-phenylenevinylene) (PPV) copolymers laterally substituted with zinc(II) phthalocyanines were synthesized by means of post-polymerization, DCC-mediated esterification reactions between hydroxy-functionalized Zn(II) phthalocyanines and carboxy-functionalized PPV copolymers.

pp. 667–673
The approach to the direct interpretation of $^{13}$C NMR of heteroleptic triple-decker (porphyrinato)(phthalocyaninate) lanthanum(III) without carbon labelling
Kirill P. Birin*, Yulia G. Gorbunova* and Aslan Yu. Tsivadze

Application of various gradient-enhanced homo- and heteronuclear correlation techniques for interpretation of $^{13}$C NMR data for lanthanum triple-decker (porphyrinato)(phthalocyaninate) is reported. Analysis of 2D correlation spectra allowed complete assignment of complicated $^{13}$C spectrum, containing resonances of four CH$_2$-groups, six CH-groups and seven quaternary carbons.

pp. 674–677
Porphyrin analogs bearing exocyclic double bonds at meso-positions: bis(meso-diethylmalonylidene)-(1,4-naphthi)thiaporphyrin
Jaeduk Yoo, Hyun-Jin Kim, Han-Je Kim and Chang-Hee Lee*

*Meso-diethylmalonylidene-(1,4-naphthi)thiaporphyrin containing exocyclic C=C double bonds at meso-positions has been synthesized and characterized. The compound undergoes initial protonation at the α-position of the diethylmalonyl group with large red shifted absorption maxima. The second protonation occurs at a meso-position to give a species with broken cross-conjugation.

pp. 678–685
Synthesis and photophysical properties of doubly porphyrin-substituted cyanine dye
Kazuya Ogawa*, Yasunori Nagatsuka and Yoshiaki Kobuke*

A new porphyrin-(cyanine dye) composite, where two porphyrins are bridged by cyanine dye though triple bonds, was synthesized. UV-vis absorption and fluorescence properties were investigated. The effective two-photon absorption cross-section values were measured by using a nanosecond open aperture Z-scan method.
Tetrabenzodiazaporphyrin: the semiconducting hybrid of phthalocyanine and tetrabenzoporphyrin
Tetsuo Okujima*, Guangnan Jin, Saika Otsubo, Shinji Aramaki, Noboru Ono, Hiroko Yamada and Hidemitsu Uno

We have successfully synthesized (tetrabenzodiazaporphyrinato)copper(II) (TBDAP) based on the retro Diels-Alder reaction of the bicyclo[2.2.2]octadiene-fused precursor which was prepared by the reaction of the corresponding dipyromethane with sodium nitrite in acetic acid/ethanol in the presence of copper(II) acetylacetonate. The solution-processed fabrication produced TBDAP-OFET with $\mu$ of $6.9 \times 10^{-4}$ cm$^2$.V$^{-1}$.s$^{-1}$.

A new method for the synthesis of meso-brominated $\beta$-substituted porphyrins
Hasrat Ali and Johan E. van Lier*

Reaction of derivatives of various Ni porphyrins with N-bromosuccinimide and triethylamine trihydrofluoride gave mono- through tetra-meso-brominated derivatives as the principal products together with $\beta$-brominated porphyrins as secondary products. The central metal ion was shown to play a major role in these reactions.

Synthesis and crystal structure of a novel phthalocyanine-calixarene conjugate
C. Grazia Bezzu, Madeleine Helliwell, Benson M. Kariuki and Neil B. McKeown*

The synthesis and crystal structure of a novel phthalocyanine-calixarene conjugate (Pe-Calix), derived from a calixarene-based phthalonitrile (Pn-Calix), is reported. The full cone configuration of the calixarene unit is retained and thus is suitable for the binding of appropriate chemical species. This new conjugate may find application as a molecular sensor.

DNA-Interaction and nuclease activity of porphyrin-hydroxamic acid derivatives in the presence of lanthanides
Marie-Cécile Chalbot, Leonidas Gryllos, Kosmas Kefokeris, Nikos Manoussakis, Catherine Verchère-Béaur, Martine Perrée-Fauvet* and Athanassios G. Coutsolelos*

Different DNA-interaction modes were observed depending on the number of charges and hydroxamic acid functions. The nuclease activity in the presence of lanthanides was shown to depend on the $1/r_0$ ratio and the nature of the lanthanide ion, and the optimum conditions are depicted after a systematic study.
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pp. 718–726
New heterogeneous photosensitizers with phthalocyanine molecules covalently linked to aminopropyl silica gel

New heterogeneous photosensitizers were synthesized, in which phthalocyanines of zinc and aluminum, tetrasubstituted at non-peripheral positions with modified thiophenyl groups, were grafted to aminopropyl silica gel. These silica-bound cationic phthalocyanines produce singlet oxygen and display photobactericidal activity.

pp. 727–741
Steric bulkiness of pyrrole substituents and the out-of-plane deformations of porphyrins: nickel(II) octaisopropylporphyrin and its meso-nitro derivative
Raid Haddad, Yi Lu, J. Martin E. Quirke, Patrick Berget, Lisong Sun, James C. Fettinger, Kevin Leung, Yan Qiu, Neil E. Schore, Frank van Swol, Craig J. Medforth and John A. Shelnutt*

Isopropyl substituents at the β-carbons of porphyrins are sufficient to cause large out-of-plane porphyrin distortions even in the absence of substituent groups at the meso bridging carbons. Molecular simulations, resonance Raman spectroscopy, and X-ray crystallography of nickel(II) complexes of octa(isopropyl)porphyrin and meso-5-nitro-octa(isopropyl)porphyrin reveal large out-of-plane distortions induced by the β-isopropyl groups but the macrocycle distortion fails to lead to a single strongly favored conformer.

pp. 742–747
Boronic esters of a porphyrazine and its precursor
Şükran Cenikli Başeren, Şennur Özçelik and Ahmet Gül*

Phenylboronic acid esters of an unsaturated precursor 1,2-dicyano-1,2-bis(2-hydroxyethylthio)ethylene and the magnesium porphyrazine derived from it were prepared either by refluxing a mixture of the reagents in chloroform in the presence of molecular sieve or by solvent-free heating in an oven under reduced pressure. The two novel compounds were characterized by some spectral experiments.

pp. 748–755
Iodine doping of substituted μ-carbido iron diphthalocyanines
Gloria Zanotti*, Sara Notarantonio, Anna Maria Paoletti, Giovanna Pennesi and Gentilina Rossi

Hemi and amphi-substituted μ-carbido iron 1 and 2 were oxidised with I₂. The correspondent molecules were characterized with spectroscopic analyses and then their conduction properties were studied. The values obtained resulted to be considerably higher than those of their non-oxidised precursors and this behavior could be related to the role played by the pushing groups inserted in the peripheral macrocycles.