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研究課題名（和文）Linear Acene Proton Conductors for Molecular Protonics

研究課題名（英文）Linear Acene Proton Conductors for Molecular Protonics

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　3,000,000円

研究成果の概要（和文）：最大14個の窒素原子を含む一連のアセン化合物「含窒素アセン」を合成し，有機化学的解析手法および単結晶構造解析によりその構造を同定した．合成した含窒素アセンは、報告されている中で最も長い化合物である．この含窒素アセンを還元することで、窒素原子上の水素原子が非局在化することを示した．また，これらの含窒素アセン類は基板表面で自己組織化し超分子ポリマー構造を形成することを明らかにした．本研究で合成した含窒素アセン類は，その電気化学特性から有機薄膜太陽電池への応用可能性を有するとともに，プロトン源または光感受性化合物存在下で有機触媒として応用可能であることを示した．

研究成果の概要（英文）：A class of linear acenes containing up to 14 nitrogen atoms has been prepared. These are the longest ‘pyrazinacene’ compounds prepared to date. The compounds have been characterized by chemical methods and crystallography. If compounds contained reduced rings (i.e. have hydrogen atoms) they were found to be delocalized, as predicted. Several compounds were studied for self-assembly on surfaces and were found to form polymeric structures. Some of the compounds were found to be useful for solar cell applications. The compounds were also found to be highly useful as organic catalysts based on the presence of the exchangeable protons and photosensitivity, as discovered in this work.

研究分野：　化学

キーワード：　Acene　Proton conductor　Pyrazinacene

１．研究開始当初の背景

Acenes, such as pentacene, are an important class of material for organic electronics. Pentacene has been used to prepare organic field effect transistors having charge carrier mobilities in excess of 5 $cm^2/V \cdot s$, exceeding that of amorphous silicon. For this reason, there has been great interest in synthesis of acene derivatives both domestically and in the broader chemistry community. Several groups have reported extended acenes, acenes with appended groups for solution processing and also heteroatom substituted acenes.

In previous work, we have developed new syntheses of nitrogen atom substituted acenes which exhibit a variety of properties based on their differences with normal CH-only acenes and for which we coined the original term 'PYRAZINACENES'. In particular, we have observed that extended linear reduced N-subsituted acenes ([H]-pyrazinacenes) undergo tautomerization involving intra- molecular proton transfer between nitrogen atoms of their acene skeletons. We have also determined using density functional theory (DFT) calculations that proton transfer is coupled with electronic orbital structure.

２．研究の目的

The purpose of this research is to develop the science of nitrogen-substituted acene (pyrazinacene) derivatives as protonic materials (at the single molecule and bulk levels). It will lead to advances in basic scientific understanding of tautomeric processes and its potential for application in high level molecular electronics and for advanced applications as protonic materials, for instance, in molecular electronic applications.

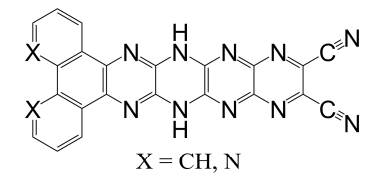
３．研究の方法

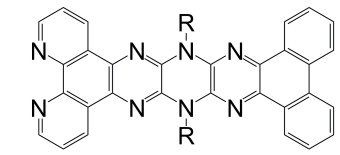
Pyrazinacenes were prepared by organic synthetic methods based on our previous work, and their structures characterized using NMR spectroscopy and other chemical analytical methods as well as by X-ray crystallography where possible. The compounds were also analyzed using DFT methods and cyclic volatammetry. Some of the compounds were developed for solar cell applications while others were investigated for their self-assembly properties including in solution and on surface.

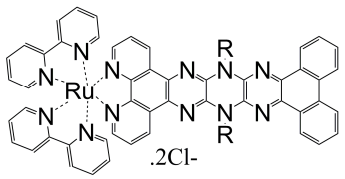
４．研究成果

The results can be divided into four areas: (a) synthesis, (b) dye sensitized solar cells, (c) self-assembly on surface, (d) self-assembly in solution and.

(a) Synthesis. Preparation of the compounds was successful leading to longest ever prepared pyrazinacene compounds as well as phenanthroline compounds. For the latter, a one-step synthesis was discovered leading directly to octaazapentacene derivatives. The first ever synthesis of decaazapentacene was successful and included the preparation of octaazatetracene which had also never been prepared. Monomer compounds for synthesis of polymer materials were prepared. N-substitution by alkylation was used as a method to investigate proton mobility in these compounds.







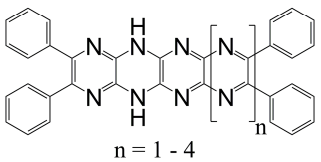


Figure 1. Compounds prepared in this work

(b) Dye-sensitized solar cells. Compounds substituted with phenanthroline groups were used to prepare Ru-containing dye sensitzers and were incorporated in typical Graetzel-type cells. These gave modest performance but the results successfully indicate the potential of

using these compounds for photovoltaic applications.

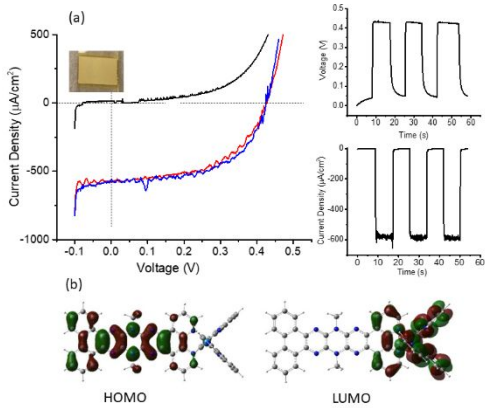
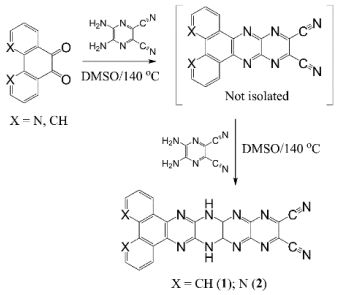


Figure 2. Device characteristics of DSSC from Ru-pyrazinacene. (a) I-V curves and on/off characteristics. (b) HOMO-LUMO structures indicating push-pull action.

The one step synthesis of unsymmetrical octaazapentacene from commercially availavle precursors was also discovered and developed:



(c) Self-assembly on surface.
Symmetrical and unsymmetrical compounds were assembled into films on surfaces.

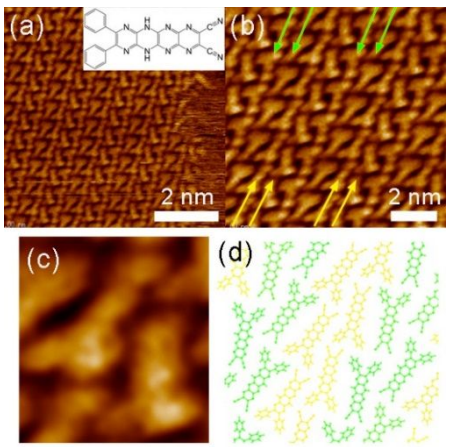


Figure 3. Monolayer films with unique structures from pyrazinacenes.
Figure 3 reveals the unique antiparallel bimolecular assembly of unsymmetrically-substituted molecules. For symmetrically substituted ones (octaazatetracene), different features were found (see Figure 4). Molecules assembled based on C-H…N hydrogen bonding and were cyclodehydrogenated to polyaromatic acenes after high temperature annealing. These features are important for their proton conducting properties.

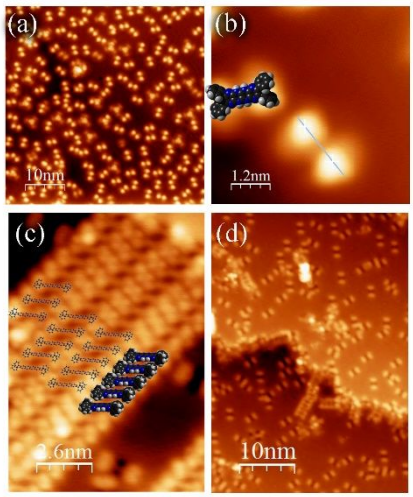


Figure 4. Scanning tunneling microscopy images of octaazatetracene revealing self-assembly of the molecules into polymeric lines.

(d) Self-assembly in solution.
In this work, long pyrazinacenes composed of up to 7 pyrazine groups have been synthesized. Because of their amphiphilic character, they were found to self-assemble into fibre and sometimes helical fibre structures.

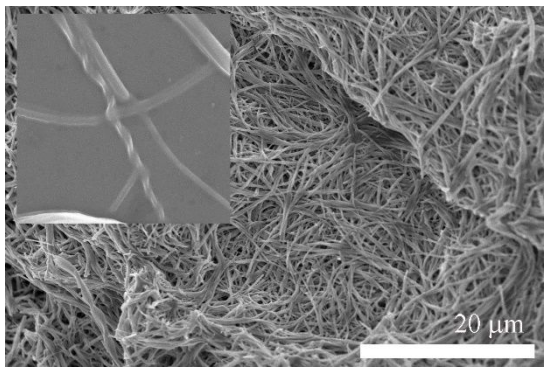


Figure 5. Scanning electron microscopy of pyrazinacene self-assembled fibres. Inset shows spontaneously helical fibre formation.

The successful synthesis of this family of materials has allowed us to investigate the self-assembly properties, the tautomeric properties of the compounds and electronic properties especially towards energy-related applications. The characterization of these materials is still ongoing and it is expected that further breakthroughs will be made in

applications related to the structures and properties of these novel compounds.

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

〔雑誌論文〕（計 8 件）

1. “Thermally-activated Self-assembly and *In Situ* Oxidation of a Reduced Decaazapentacene.” D. Miklik, S. F. Mousavi, A. Middleton, Y. Matsushita, J. Labuta, A. Ahsan, P. A. Karr, P. Svec, F. Bures, G. J. Richards, T. Mori, K. Ariga, Y. Wakayama, F. D’Souza, T. A. Jung, J. P. Hill. Submitted (2018).

2. “Phenanthroline-fused Pyrazinacenes: One-pot Synthesis, Tautomerization and a Ru(II)(2,2’-Bipy)$_2$ Derivative.” P. Svec, W. A. Webre, G. J. Richards, J. Labuta, Y. Wakayama, D. Miklík, P. A. Karr, T. Mori, K. Ariga, F. D’Souza, J. P. Hill. *Eur. J. Inorg. Chem.* (2018) in press.
DOI: 10.1002/ejic.201800283

3. “Structural Modulation of Chromic Response: Effects of Binding Site Blocking in a Conjugated Calix[4]pyrrole Chromophore.” V. Březina, S. Ishihara, J. Lang, L. Hanyková, K. Ariga, J. P. Hill, J. Labuta. *ChemistryOpen* 7, 323–335, (2018).
DOI: 10.1002/open.201800005

4. “Corrole NH-Tautomers with Significantly Different Polarity: Experimental Identification of Individual Absorption and Fluorescence Features Supported by Quantum Chemical Calculations.” J. Preiß, T. Sachse, F. Herrmann-Westendorf, T. H. Ngo, Todd Martínez, B. Dietzek, J. P. Hill, K. Ariga, M. Kruk, W. Maes, M. Presselt, *J. Phys. Chem. A* 121, 8614–8624, (2017).
DOI: 10.1021/acs.jpca.7b08910

5. “Substrate-mediated C-C and C-H Coupling after Dehalogenation.” H. Kong, S. Yang, H. Gao, A. Timmer, J. P. Hill, O. Díaz Arado, H. Mönig, X. Huang, Q. Tang, Q. Ji, W. Liu, H. Fuchs. *J. Am. Chem. Soc.* 139, 3669–3675, (2017).
DOI: 10.1021/jacs.6b10936

6. “Novel Solid-state Luminous Composites from a Layered Inorganic-organic Monolith containing Neutral Porphyrins.” K. Fujii, J. P. Hill, H. Hashizume, S. Shimomura, K. Ariga, T. Ando. *J. Mater. Sci.* 52, 12156–12169, (2017).
DOI: 10.1007/s10853-017-1305-1

7. “Mesomorphic Fluorescent Pyrazin acenes.” G. J. Richards, S. Ishihara, J. Labuta, D. Miklik, T. Mori, S. Yamada, K. Ariga, J. P. Hill. *J. Mater. Chem. C* 4, 11514–11523, (2016).
DOI: 10.1039/c6tc04628b

8. “Anion Binding, Electrochemistry and Solvatochromism of ß-Brominated Oxoporphyrinogens.” W. A. Webre, J. P. Hill, Y. Matsushita, P. A. Karr, K. Ariga, F. D’Souza. *Dalton Trans.* 45, 4006–4016, (2016)
DOI: 10.1039/c5dt04258e

〔学会発表〕（計 13 件）

1. J. P. Hill, Self-assembly of Porphyrin Nanostructures, 23rd Intl Conf. on Nanomaterials and Nanotechnology, 15-16/03/2018, London, UK.

2. J. P. Hill, Porphyrin Clamp, Tripod and Rotor in Surface Assemblies, Int. Conf. on Advances in Polymer Science and Technology, 23-25/11/2017, Delhi, India.

3. J. P. Hill, Pyrazinacenes, Porphyrins and Oxoporphyrinogens, Int. Conf. on Functional Nanomaterials and Nanotechnology, 10-13/10/2017, Kathmandu, Nepal.

4. J. P. Hill, Pyrazinacenes and Oxoporphyrinogens, Congress of the Slovak Chemical Society, 11-15/09/2017, Smokovec, Slovakia.

5. J. P. Hill, Pyrazinacenes and Oxoporphyrinogens, 231st Electrochemical Society Meeting, 28/05/2017 – 01/06/2017, New Orleans, USA.

6. J. P. Hill, Pyrazinacenes and Oxoporphyrinogens: Luck and Design in Chromophore Synthesis, Collaborative Conf. on Organic Synthesis, 13-17/03/2017, Hanoi, Vietnam.

7. J. P. Hill, Self-assembling pyrazinacenes: structure and properties, OrgSyn50, 26-27/02/2017, Manchester,

U.K.

8. J. P. Hill, Porphyrin Clamp, Tripod and Rotor in Surface Assemblies, IUMRS-ICYRAM 2016, 11-15/12/2016, Bangalore, India.

9. J. P. Hill, Porphyrin Clamp and Tripod for Surface Assembly, ICPP-9, 03-08/07/2016, Nanjing, China.

10. J. P. Hill, Interactions of Antioxidant-Substituted Macrocycles, 229th Electrochemical Society Meeting, 29/05/2016 – 02/06/2016, San Diego, USA.

11. J. P. Hill, Pyrazinacenes, porphyrins and nanoparticles: liquid crystals and self-assemblies, EMN Meeting on Liquid Crystals, 16-19/02/2016, Orlando, USA.

12. J. P. Hill, Porphyrins, Pyrazinacenes and Oxoporphyrinogens: Supramolecular (and other) Effects, 5th NIMS-UR1-CNRS-Saint Gobain Workshop, 11-13/10/2015, University of Renne, France.

13. J. P. Hill, Porphyrins, Pyrazinacenes and Oxoporphyrinogens: Self-assembly Control and Effects, Self-assembly & Self-organization in Computer Science & Biology, 28/09/2015 – 02/10/2015, Saarbrucken, Germany.

〔図書〕（計　1　件）

1. “Tautomerism in Oxoporphyrinogens and Pyrazinacenes” J. P. Hill, J. Labuta, G. J. Richards, Y. Xie, K. Ariga. Tautomerism Ideas and Applications Editor: Liudmil Antonov. Publisher: Wiley-VCH, (2016) pp. 203–228

〔産業財産権〕

○出願状況（計　　件）

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発明者：
権利者：
種類：
番号：
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○取得状況（計　　件）

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発明者：
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〔その他〕
ホームページ等

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