

# Digest

J. Jpn. Soc. Colour Mater., 96 [4], 131–136 (2023)

## Pyrazinacenes as a New Class of Highly Fluorescent REDOX Active Chromophores

Gary J. RICHARDS<sup>\*,†</sup>, Keita AOKI<sup>\*</sup>, Daiki AKIBAYASHI<sup>\*</sup>, Majid TAMBOLI<sup>\*</sup>, Jonathan P. HILL<sup>\*\*</sup> and Akiko HORI<sup>\*</sup>

<sup>\*</sup>Department of Applied Chemistry, Graduate School of Engineering and Science, Shibaura Institute of Technology,  
307 Fukasaku, Minuma-ku, Saitama-shi, Saitama 337-8570, Japan

<sup>\*\*</sup>Functional Chromophores Group, International Center for Materials Nanoarchitectonics, National Institute for Materials Science,  
1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

<sup>†</sup>Corresponding Author, E-mail: richards@shibaura-it.ac.jp

(Received December 1, 2022; Accepted December 27, 2022)

### Abstract

Pyrazinacenes consist of rectilinearly fused 1,4-pyrazine units and can be considered as analogues of the well-studied acene family of compounds with the apical CH units replaced with nitrogen atoms. Herein we discuss the family of pyrazinacene compounds that have been developed recently paying particular attention to their photophysical properties. We show that REDOX properties are dependent on the number of fused rings in the respective pyrazinacenes, and that in their reduced forms, pyrazinacenes are typically highly fluorescent species with solution fluorescence quantum yields typically above 50%, even in extended or deprotonated systems where emission in the near infrared (NIR) region can be elicited.

**Key-words:** Pyrazinacenes, Acenes, REDOX, Near infrared, Fluorescence

### 1. Introduction

Acenes<sup>1,2)</sup>, consist of rectilinearly fused benzene rings and are a class of compounds that has attracted significant interest due to potential applications in molecular electronics as organic field-effect transistors or organic photovoltaics<sup>3-6)</sup>. Many acene derivatives have been investigated in part to account for their intrinsic disadvantageous properties including their low stability (especially of the higher acenes) and processability issues involving their low solubility<sup>7-9)</sup>. Acenes are electron-rich molecules whose aromaticity decreases with increasing multiplicity of fused rings so that higher acenes are susceptible to oxidative processes leading to different degradation products depending on the substrate<sup>10,11)</sup>. The low stability of acenes has been ameliorated to some extent by various strategies such as the introduction of bulky substituents at reactive positions<sup>12-14)</sup> or by introducing heteroatoms<sup>15)</sup>, in particular, nitrogen<sup>16)</sup>,

leading to closely related families of compounds known as the azaacenes<sup>17)</sup> or *N*-heteroacenes<sup>18,19)</sup>. Here, we review recent investigations into the photophysical properties of compounds in which all the apical C-H groups of hydrocarbon acenes are replaced with nitrogen atoms. This family of compounds, for which we have coined the term “pyrazinacenes”<sup>20,21)</sup>, have properties that depart significantly from those of conventional acenes or azaacenes. The relative structures of pyrazinacenes as compared to their acene congeners are illustrated in **Scheme 1a**.

There are many reports of acenes containing one, two or three pyrazine rings and some of those most studied include fluoiflavine<sup>22)</sup> and fluorubine<sup>23)</sup> (Scheme 1b) of which various substituted derivatives have been reported<sup>24,25)</sup>. However, there have been few reports of pyrazinacenes consisting of more than three consecutively fused pyrazine rings. Prior to our contribution<sup>26)</sup>, the longest known pyrazinacenes were the doubly reduced dodecaazahexacenes (Scheme 1c) reported by Stöckner and co-workers<sup>27)</sup>. The synthetic route to these compounds leads directly to the tetra-*N*-arylated species. Solutions of these compounds exhibited fluorescence at  $\lambda_{\text{max}} = 522 \text{ nm}$  with fluorescence quantum yields of 35% and a small Stokes shift of 5 nm.

Our synthetic route to pyrazinacenes<sup>20)</sup> involves a double nucleophilic aromatic substitution of electron-deficient 2,3-dicyano-1,4,5,8,9-tetraazanaphthalene moieties using aromatic *o*-diamines as shown in Scheme 1d. Using this approach, we have synthesized a large family of pyrazinacene compounds that feature between 3 and 7



〔氏名〕 リチャーズ ゲーリー ジェームズ  
〔現職〕 Associate Professor, Department of Applied Chemistry, Shibaura Institute of Technology  
〔経歴〕 From 1997 - PhD in Organic Chemistry, University of Hull, UK. 2001 – Post-doctoral Research Associate, Oxford University, UK. 2007 – Research scientist, National Institute of Materials Science, Japan. 2013-2014 – Assistant Professor, Tsukuba University. 2014-2020 – Associate Professor, Ochanomizu University. Current position from 2020.

【Figures and illustrations】 Figures and illustrations published in black and white in the journal can be seen in color at our public website 「J-STAGE」. Please make use of it.