Structural Dynamics Research Group

Katarzyna N. Jarzembska and Radosław Kamiński

Piotr (Piotrek) Łaski (PhD stud.), Radosław (Radek) Kamiński (co-PI), Katarzyna (Kasia) Jarzembska (PI, the boss), Krystyna (Krysia) Deresz (PhD stud.), Kinga Potempa (PhD stud.), Bartosz (Bartek) Szymański (MSc stud.), Vishnu Vijayakumar Syamala (post-doc), Dariusz (Darek) Szarejko (developer); *missing here:* Jakub (Kuba) Drapała (PhD stud.), Kacper Paszczyk (MSc stud.), Patryk Borowski (PhD stud.), Róża Okoń (*former* BSc stud.)

Research topics

Photocrystallography – ultrafast time-resolved and steady-state experiments

Transition-metal complexes and photoactive functional materials

High-pressure X-ray diffraction and spectroscopy

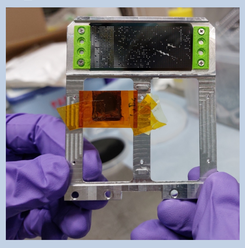
Crystallographic software development

Instrumentation design and construction

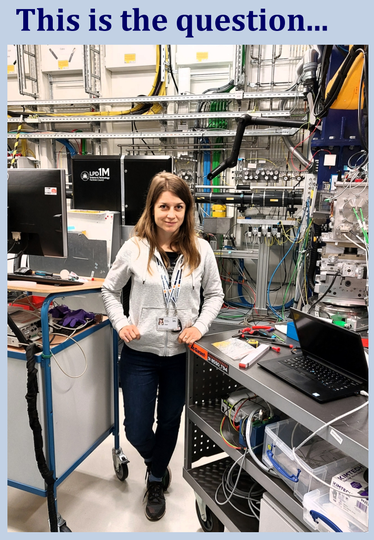
We know where to look for good research!

Maksio, Stasio

This is pure science!

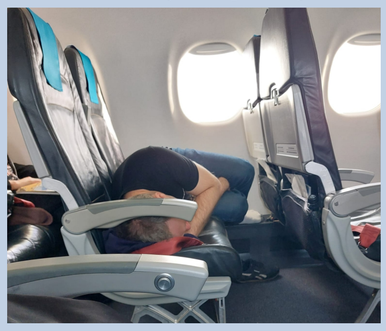


OK, where to start... or rather, what to break? This is the question...



Kasia at the European XFEL

Radek (on a plane)



A typical way Radek sleeps onboard...

Ready for driving to Elettra for exciting HP X-ray science

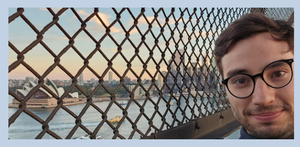
Radek, Vishnu, Patryk & Kinga (still in Slovenia though)

Apparently the sea down under also sticks to the Earth sphere

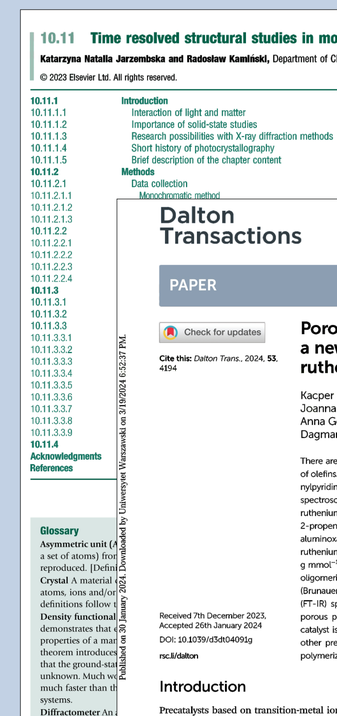
Bartek, Kinga & Piotrek (Melbourne)

Our dream team in Australia

Piotrek near Sydney



Spot the famous opera house



Glossary

Asymmetric unit (
a set of atoms) fro
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Crystal A material
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Introduction 275
Interaction of light and matter 275
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Research possibilities with X-ray diffraction methods 276
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Methods 277
Data collection 278
Monochromatic method 278
11.4 Acknowledgments
References

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[d]Institute of Chemistry, Jan Kochanowski University, Uniwe
Poland

† Electronic supplementary information (ESI) available,
and crystallographic data in CIF or other electronic for
org/10.1039/d3dt04091g

We start doing real chemistry very early

Maksio, Radek, Stasio

Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

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Cite this: *Dalton Trans.*, 2024, **53**, 4194

Porous oligomeric materials synthesised using a new, highly active precatalyst based on ruthenium(III) and 2-phenylpyridine†

Kacper Pobłocki, [a,a] Katarzyna N. Jarzembska, [b] Radosław Kamiński, [b] Joanna Drzeżdżon, [a] Krystyna A. Deresz, [b] Dominik Schaniel, [c] Anna Got Dagmara

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ruthenium(
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Received 7th December 2023,
Accepted 26th January 2024
DOI: 10.1039/d3dt04091g
rsc.li/dalton

Published on 30 January 2024. Downloaded by Uniwersytet Warszawski on 3/19/2024 6:23:37 PM.

Introduction

Precatalysts based on transition-metal ions
designed thanks to their wide applications
polymerization of olefins.[1] Continuous deve
an increase in the global demand for high-v
intermediates, alpha- and beta-olefin poly
high-density polyethylene (HDPE), isota
(IPP), *cis*- and *trans*-polydienes, and ethylen
mers (EPE).[2–4] Large-scale polyolefins are n

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Poland

† Electronic supplementary information (ESI) available,
and crystallographic data in CIF or other electronic for
org/10.1039/d3dt04091g

CRYSTAL GROWTH & DESIGN

pubs.acs.org/crystal

Article

Impact of *Cis–Trans* Isomerism on Crystal Packing and Photo-Activity of a Cobalt(III) Room-Temperature Photoswitch

Patryk Borowski, Katarzyna N. Jarzembska,* Radosław Kamiński,* Krzysztof Durka, and Dominik Schaniel

Cite This: *Cryst. Growth Des.* 2023, 23, 5986–5997

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ABSTRACT: A bis(acety
(III) coordination comp
toward photoswitching p
isomers, *cis* and *trans*, dep
two acetylacetone ligand
both isomers were obta
photoswitchable in the so
a lesser extent at lower te
irradiation (365–405
spectroscopic results, the
ambient conditions with
reaching ca. 80%. The re
isomer is stable at 100 K,
relaxation is observed 7 h
continuous illumination
around 60%. In turn, the
state spectroscopic and
differences in photoactivit
on steric and energetic fa

1. INTRODUCTION

Conscious design of fu
desired properties, which
easy to synthesize, rem
challenge. In this resp
compounds constitute an
to their rich electronic pr
tuned by structural cha
exchanging metal center
already found important r
biological markers, or in

The photoactivity of va
in many different wa
luminescence, and othe
formations upon light
molecular photoswitches
reactions, such as isom
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SO_2) constitute a good e
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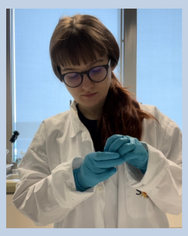
CAUTION HOT



Pellet, pellet on the 'wall', who's the fairest of them all?

Gainig a new perspective!

Hot Paper

Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202302629

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European Chemical Societies Publishing

www.chemeurj.org

Interrelations between Linkage Isomers of an Efficient Square-planar Nickel(II) Nitrite Photoswitch in the Solid State

Kinga Potempa,[+,a] Krystyna A. Deresz,[+,a] Joanna Jankowska,[a,c] Katarzyna N. Jarzembska,*[a] Adam Krówczyński,[a] Artem Mikhailov,[b] Dominik Schaniel,[b] and Radosław Kamiński[a]

An efficient nitrite nickel(II) photoswitch, with the 1-phenyl-2-hydroxyimino-3-[(2′-dimethylamino)ethyl]imino-1-propanone moiety used as the ancillary ligand, is reported. In the ground-state ('dark') crystal structure, the studied compound exists predominantly as the nitro-(η^1-NO_2) isomer, however, traces of the *exo*- and *endo*-nitrito-(η^1-ONO) forms are detected both at 100 K (4–5% each) and under ambient conditions (~9% each). When excited with the 405–530 nm LED light, the nitro-to-nitrito isomerization takes place. The total conversion exceeds 90%. The *exo*-nitrito linkage isomer constitutes the dominant photo-generated form, whereas the relative population of both nitrito species depends on temperature. The reaction is fully reversible and reproducible. The photo-products are stable up to 200 K. The system constitutes a good model case for the reaction mechanism studies. Thus, experimental and theoretical investigations on the photo-isomerism were conducted and are presented in detail. Eventually, the nitro→*exo*-nitrito→*endo*-nitrito reaction pathway is proposed.

Introduction

Molecules that can undergo structural transformations upon exposure to light are classified as photoswitches.[1,2,3] Thanks to their capability to interconvert between two or more (meta)stable states, they may find wide applications in materials science, optoelectronics, or biology.[4] Molecular photoswitches are typically organic molecules with extended aromatic systems responsive to light.[5] Nevertheless, transition-metal complexes possessing ambidentate ligands, such as NO, NO_2, or SO_2[2,6,7,8–11,12–15] constitute a promising and readily modifiable group of this kind of compounds.[9] The ambidentate ligands are the key fragments of these molecules because they can bind to a metal center in multiple ways which can be controlled optically.[16]

In the view of the above, the nitrite group constitutes an interesting moiety as it may adopt up to nine different binding modes,[17] some of which can interconvert one into another under certain conditions. In the case of mono-nuclear transition-metal complexes, four linkage isomers can be observed, i.e. nitro-(η^1-$N(O)_2$), *exo*-nitrito-(η^1-ONO), *endo*-nitrito-(η^1-ONO), and κ-nitrito-(η^2-O_2N) forms (Scheme 1).[9,17] Up to date, numerous photoswitchable nitrite transition-metal coordination systems have been reported.[8,9,11,15,18–20,21] There are, though, rather limited examples of high-conversion photoswitches of this kind, and/or complexes which work at higher temperatures.[10,11,13–15,22–24] Furthermore, an aspect which is still under debate is the mechanism of light- and thermally-induced transformations between linkage isomers. There are few papers which undertake this issue supporting experimental presumptions with theoretical modelling. The articles published by Muya et al.[25] and Skelton et al.[26] are devoted to octahedral nitro complexes of cobalt(III) and nickel(II), respectively, whereas there is only one paper discussing a square-planar nitro Ni^{II} complex.[22] In the case of the octahedral Ni^{II} compound, which exhibits a triplet electronic configuration in the ground state, theoretical modelling results indicated that the nitro-to-*endo*-nitrito transformation occurs first and then the *endo*-nitrito product can isomerize further, with lower energy barrier, to the *exo*-nitrito form. There was no evidence of a direct reaction pathway connecting the *exo*-nitrito and nitro forms, the reasons for which were not clear. For the analyzed singlet octahedral

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202302629

Scheme 1. Schematic diagram of possible NO_2-group binding modes in mono-nuclear complexes (M = metal center). Note the κ-nitrito isomer was not observed in this study.

Find ~~Wally~~ Kasia at this kick-off XFEL meeting

Spot the famous opera house

Leisure and pleasure

Ania Hoser, Maura Malińska, Radek, Ania Makal, Kasia, Kuba Wojciechowski

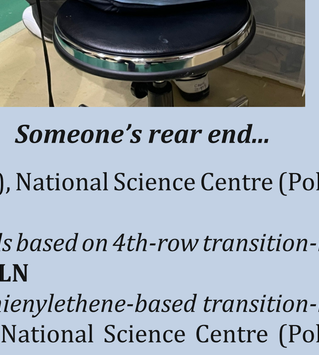
All laboratory 'equipment' must be properly labelled

Vishnu

Happy or not? Can't really say...

Someone's rear end...

Very true, no doubts



Krysia's hand

Strange Case of Dr Jekyll & Mr Hyde

Darek in the middle of nowhere

Krysia during her NAWA project in Nancy, France

More new results? Coming up!

Vishnu & Miłosz Siczek (Wrocław trip)

This is how real crystallographers take selfies!

materials

MDPI

Article

Catalyt
and cob
and 4-A

Jacek Malino
Przemysław

Inorganica Chimica Acta 565 (2024) 121995

Contents lists available at ScienceDirect

Inorganica Chimica Acta

ELSEVIER

Polyhedron 230 (2023) 116210

Contents lists available at ScienceDirect

Polyhedron

ELSEVIER

[8]Ferrocenophanes with
Synthesis via olefin meta

Karol Rawiak[a], Maria Mazur[a,]
Piotr Paluch[c], Piotr A. Guńka[a],
Włodzimierz Buchowicz[a,*]

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[c] Polish Academy of Sciences, Centre of Molecular and
[d] Department of Chemistry, University of Warsaw, Żwi

ARTICLE INFO

Keywords:
[8]Ferrocenophane
Grubbs' catalyst
Olefin metathesis
Single crystal X-ray structure
Variable temperature NMR

1. Introduction

Olefin metathesis has been successfull
ferrocenophanes (*ansa*-ferrocenes) for twe
of 1,1′-diallylferrocenes (Scheme 1a) with
catalysts [Ru(=CHPh)Cl$_2$(PCy$_3$)$_2$] (**GI**) resp
ferrocenophanes with the (*Z*)-configurati
bon–carbon double bonds [3,4]. More rec
rocenes (Scheme 1b), in the presence o
Cl$_2$(PCy$_3$)(SIMes)] (**GII**), yielded [6]ferroc
of the bridge depending on the type of sub
[5].

Under similar conditions, 1,1′,3,3′-tet
provided axially chiral *diansa*-metal
allylferrocene underwent a combination
closing reactions [7]. Moreover, applic
catalysts resulted in kinetic resolu
1,2-diallylferrocenes (Scheme 1c) [8]. R
was also accomplished in titanocene
[4,9,10]. Synthetic utility of all-carbon
ferrocenophanes was described in ou

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Citation: Malinow
J.; Jarzembska, K.N
Rybiński, P.; Gawd
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Complexes of chro
cobalt(II) with Nitr
Dipicolinate, and 4
Materials **2023**, *16*, 3
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Received 8 September 2022; Accepted
Available online 18 November 2022
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Chelidamic acid taut
crystal structure, spe

Agnieszka Wojciechowska
András Gorzsás[d], Ülo Kers

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[b] Institute of Low Temperature and Structure
[c] Department of Chemistry, University of War
[d] Department of Chemistry, Umeå University,
[e] Department of Chemical and Metallurgical E
[f] Department of Physical and Quantum Chemi
Poland
[g] Faculty of Chemistry, University of Wrocław

ARTICLE INFO

Keywords:
Tautomers of chelidamic acid
Copper(II) complexes
Crystal structures
Spectroscopy (FT-IR, Raman, NIR-Vis-UV, E
Theoretical calculations

1. Introduction

4-hydroxypyridine-2,6-dicarbox
acid (H_3L = H_3cda = chel), acts as
one N and three O donor atoms, cap
[1–44]. A rigid 120° angle betwee
carboxylic groups leads to a variet
starting from typical tridentate (O
structures [1,4,5b-c,8–10,11b,12,
well as bridging via the carboxyl
nated 4-hydroxy oxygen, lead
[2,3,5a,13,14,17,40–42,44].
Chelidamic acid can exist in tw

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NJC

ROYAL SOCIETY OF CHEMISTRY

PAPER

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Cite this: *New J. Chem.*, 2024, 48, 2416

The effect of rigidity on the emission of quadrupolar strongly polarized dyes†

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Received 28th November 2023,
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Hybrid dyes comprising 1,4-dihydropyrrolo[3,2-*b*]pyrrole and two strongly electron-withdrawing benzoxadiazole substituents, differing in their level of planarization, offer an insightful window into the interplay between internal conversion and intersystem crossing as relaxation pathways from the excited state. The emission intensity is strong for non-fused systems whilst it is minimal for fused dyes. Computational evaluation has revealed that internal conversion, and not inter-system crossing, is the main non-radiative process for planar, fused quadrupolar dyes.

Introduction

Centrosymmetric dyes with acceptor–donor–acceptor (A–D–A) and donor–acceptor–donor (D–A–D) architectures,[1–5] which form emissive CT states, can display solvatofluorochromism, caused by excited-state symmetry breaking (ES-SB).[6–10] Many new quadrupolar,[11–14] centrosymmetric systems have been reported over the last few years, but there has been no consensus on the influence of restricted rotation (rigidity) on the emission properties, ES-SB and thermodynamics of intramolecular charge transfer (ICT).[15]

In this regard we hypothesized that it could be possible to directly study the influence of restricted rotation on the fate of quadrupolar dye molecules in the excited state by bridging strongly electron-donating and electron-deficient moieties. Assessing this hypothesis requires two dyes possessing identical, quadrupolar scaffolds except for their degrees of rigidity. Designing the quadrupolar architectures, we considered several candidates for the electron-rich scaffold, but we eventually decided upon 1,4-dihydropyrrolo[3,2-*b*]pyrrole (DHPP) due to the combination of the following properties: (1) exceptionally high-lying HOMO; (2) straightforward and modular synthesis; (3) possibility of vast structural modification.[16–18] The combination of these features has been utilized several times, predominantly to decipher the fluorescence of nitro-aromatics.[19,20] Simultaneously, we reasoned that incorporation of 2,1,3-benzoxadiazole[21–24] at the strongly conjugated positions 2 and 5 of DHPP represents an optimal choice as an electron-acceptor. The versatility and generality of the multicomponent reaction affording tetraarylpyrrolo[3,2-*b*]pyrroles (TAPPs)[25] enabled us to assemble the required quadrupolar dye **1** in just one step (Scheme S1 (ESI†) and Fig. 1). Subsequently the benzo-[*c*][1,2,5]oxadiazole-4-carbaldehyde (2) was condensed with 2-bromo-4-octadecylaniline (3) affording TAPP **5**, which was subjected to intramolecular direct arylation,[26] giving almost planar quadrupolar centrosymmetric architecture **6** (Scheme 1).

The photophysical properties of dyes **1** and **6** were studied in solvents of various polarity and in the polycrystalline state

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[f] Department of Chemistry and Nanomaterials Science, Bohdan Khmelnytsky National University, 18031 Cherkasy, Ukraine

† Electronic supplementary information (ESI) available: Synthesis, compound characterization, X-ray structural data, supporting spectroscopic plots, computational details, computed spectroscopic characteristics, Cartesian coordinates for optimized structures and spectral data for all new compounds. CCDC 2288872. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3nj05467e

1

Fig. 1 Structural formula of centrosymmetric TAPP **1**.

Other smaller projects:

- ✓ Y. Jiang (**K.N. Jarzembska**, **R. Kamiński**, **P. Łaski** & **D. Szarejko** involved), R&D proposal **(in progress)**, **2022-2025**, European XFEL (Germany)
- ✓ **K.N. Jarzembska**, XPRESS beamline proposal accepted, **2023**, Elettra Synchrotron Facility (Italy)
- ✓ D. Khakhulin (**K.N. Jarzembska**, **R. Kamiński** & **P. Łaski** involved), beamtime proposal accepted, **2023**, European XFEL (Germany)

Selected distinctions:

- ✓ **K. Paszczyk**, *laureate of the Polish Crystallographic Olympic (5-th place)*, **2023**
- ✓ **K. Paszczyk**, *poster presentation award at the Polish Crystallographic Meeting*, **2023**
- ✓ **K.N. Jarzembska**, *UW Rector scientific award (2-nd grade)*, **2023**
- ✓ **R. Kamiński**, *teaching award for the new physics course (2-nd grade)*, **2023**
- ✓ **R. Okoń**, *Gold Medal in Chemistry for the BSc thesis*, **2023**
- ✓ **P. Łaski**, IDUB stipend for PhD students, **2023**

Research grants:

- ✓ **K.N. Jarzembska**, SONATA BIS, *"M:M-PROP: metallophilic interactions – allies or enemies?"* **2021** (ongoing), National Science Centre (Poland), **2,889,000 PLN**
- ✓ **K.N. Jarzembska**, PRELUDIUM BIS, *"MXO2-ISOMER: in search of colour-changing photoswitchable materials based on 4th-row transition-metal complexes with simple ambidentate ligands"*, **2020** (ongoing), National Science Centre (Poland), **532,800 PLN**
- ✓ **R. Kamiński**, OPUS, *"THIO-SWITCH: towards novel photo-active switchable materials – exploration of dithienylethene-based transition-metal complexes via advanced in situ photocrystallographic and spectroscopic approaches"*, **2020** (ongoing), National Science Centre (Poland), **1,999,880 PLN**
- ✓ R. Sobierajski (PI, PAS), W. Gawełda (co-PI, AMU), **K.N. Jarzembska (co-PI, UW)**, D. Milewska (co-PI, NCNR), Supporting the participation of Polish research teams in international research infrastructure projects, *"Support for Polish EuXFEL users – Supervision, Part II (2022–26)"*, **2022** (ongoing), Ministry of Education and Science (Poland), **10,539,719.81 PLN** (**1,622,650,00 PLN** for UW)

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