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List of Publication

*Thesis publications

*1. Two three-dimensional coordination polymers of lead (II) with iminodiacetate and naphthalene-dicarboxylate anions: Synthesis, characterization and luminescence behavior.
D. Hazari, S. K.Jana, M. Fleck, E. Zangrando, S. Dalai. *J. Solid State Chem.* 219 (2014) 43-48.

*2. Three new co-ordination polymers of zinc (II) and cadmium (II) with dicarboxylate and bipyridine ligands: Synthesis, structure and luminescence study.
D. Hazari, S. K. Jana, H. Puschmann, E. Zangrando, S. Dalai. *J. Inorg. Organomet. Polym.* 25 (2015) 1151-1159.

*3. Three Manganese(II) Coordination Polymers with Hetero Donor Ligands: Synthesis, X-ray Structures and Luminescence Properties.
D. Hazari, S. K. Jana, H. Puschmann, E. Zangrando, S. Dalai. *Tran. Met. Chem.* 40 (2015) 595-604.

*4. Structural Variability of Ag(I) Metal-Organic Networks: C−H···π and metal···π Interactions
D. Hazari, S. K. Jana, S. K. Seth , H. Puschmann, S. Dalai. *J. Coord. Chem.* 69 (2016) 562 – 573.

*5. 1D lead(II) coordination chains with carboxylate containing ligands. A rare example of polyrotaxane 1D→1D interpenetrated coordination polymer
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6. Synthesis, characterization, luminescent and thermal properties of a hybrid inorganic-organic polymeric framework formed by lead(II) pyridinecarboxylate
A. Rana, M. Bera, D. S. Chowdhuri, D. Hazari, R. J. Butcher and S. Dalai. *J. Inorg. Organomet. Polym.* 21 (2011) 747-753.

7. 3D Silver(I)-Diglycolate Coordination Polymer with Short Ag-Ag Bond
M. Bera, A. Rana, D. S. Chowdhuri, D. Hazari, H. Puschmann, S. Dalai. *J. Inorg. Organomet. Polym.* 22 (2012)244-252

8. 3D coordination network of Ag(I) ions with μ_3-bridging melamine ligands
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9. Three dimensional silver(I)-thiodiglycolate coordination polymer with weak Ag-Ag bond M. Bera, A. Rana, D. S. Chowdhuri, D. Hazari, S. K. Jana, H. Puschmann, S. Dalai *J. Inorg. Organomet. Polym.* 22(4) (2012) 897-902.

10. Synthesis, Crystal Structure, Thermal and Luminescent Characterization of Two New 3D Cadmium–Carboxylate Framework

D. S. Chowdhuri, M. Bera, A. Rana, D. Hazari, S. K. Jana, E. Zangrando, S. Dalai. *J. Inorg. Organomet. Polym.* 22(5) (2012) 963-972.

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M. Bera, A. Rana, D. S. Chowdhuri, D. Hazari, S. K. Jana, H. Puschmann, S. Dalai. *J. Inorg. Organomet. Polym.* 22(5) (2012)1074-1080.

12. Synthesis, crystal structure, thermal and photoluminescence properties of Cd carboxylate coordination polymers: a new 2D structure and a reinvestigation of Cd tartrate
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13. Two new metal-organic coordination polymers of lead with O-, N-donor ligands: Synthesis, characterization, luminescence and thermal behavior
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14. 2D and 1D coordination polymers of Ag(I) ions with 2,6-naphthalenedicarboxylate and N-donor coligands
M. Bera, S. K. Jana, D. Hazari, A. Rana, D. S. Chowdhuri, H. Puschmann, E. Zangrando, S. Dalai. *J. Inorg. Organomet. Polym.* 23 (2013) 325-332.

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16.Topological aspects of lanthanide–adipate–aqua compounds: Close packed and open framework structures
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Two three-dimensional coordination polymers of lead(II) with iminodiacetate and naphthalene-dicarboxylate anions: Synthesis, characterization and luminescence behavior

Debdoot Hazari [a], Swapan Kumar Jana [a], Michel Fleck [b], Ennio Zangrando [c], Sudipta Dalai [a,*]

[a] *Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapore 721 102, West Bengal, India*
[b] *Institute of Mineralogy & Crystallography, University of Vienna, Geozentrum, Althanstr. 9, A-1090 Vienna, Austria*
[c] *Department of Chemical and Pharmaceutical Sciences, University of Trieste, 34127 Trieste, Italy*

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ABSTRACT

Two lead(II) compounds $[Pb_3(idiac)_3(phen)_2(H_2O)]\cdot 2(H_2O)$ (**1**) and $[Pb(ndc)]_n$ (**2**), where H_2idiac = iminodiacetic acid, phen = 1,10-phenanthroline and H_2ndc = naphthalene-2,6-dicarboxylic acid, have been synthesized and structurally characterized. Single crystal X-ray diffraction analysis showed that compound **1** is a discrete trinuclear complex (of two-fold symmetry) which evolves to a supramolecular 3D network via π–π interactions, while in compound **2** the naphthalene dicarboxylate anion act as a linker to form a three dimensional architecture, where the anion adopts a bis-(bidentate bridging) coordination mode connecting four Pb(II) centers. The photoluminescence property of the two complexes has been studied.

1. Introduction

Metal–organic frameworks (MOFs)/coordination polymers (CPs) with variety of metal ions having fascinating structures and interesting material properties, like ion exchange, catalysis, opto-electronic, electrical, magnetic devices and many more, have attracted intense attention in recent time [1–3]. It is an established fact that large variety of coordination networks having interesting topologies and preferred properties can be synthesized by planned combination of organic species and metal ions. A literature study reveals that till date most of the efforts have been devoted to the study of transition metal coordination polymers [4–6]. On the contrary, relatively less attention has been paid to coordination polymers of main group metal ions, however, they have great applications in the area of electroluminescent devices [7] or organic light-emitting diode (OLED) technology [8].

Lead(II) coordination polymers are interesting for their unexpected structural networks in comparison to the coordination polymers formed by transition metal ions and became a topic of interest for the researchers due to two major points: (i) large ionic radius of lead(II) induces a wide range of coordination numbers (2 to 10), which in turn opens-up the possibility for the construction of a variety of Pb(II) functional materials [9] and (ii) the presence of $6s^2$ outer electrons have a unique influence on the overall geometry of the lead's coordination sphere. Such intrinsic feature of Pb(II) finds great application in coordination chemistry, photophysics and photochemistry [10]. The presence of lead in the environment is due to its frequent industrial applications. Thus understanding of the coordination properties of lead(II) ion is vital to realize the toxicological properties of this metal and the development of efficient chelating agents for the remediation of polluted water and soil [11,12].

In continuation to our work on coordination polymers with Pb(II) metal ion [13–16], in this paper we describe the use of iminodiacetic and naphthalene-2,6-dicarboxylic acid as ligand (Scheme 1) for the construction of two novel compounds of lead(II). Literature study revealed that the use of iminodiacetic acid as organic ligand with a variety of metal ions or combination of different metal ions led to a number of compounds having different interesting structural, chemical and physical properties.

In fact from a structural point of view a novel family of lanthanide hybrid frameworks was synthesized with iminodiacetic acid showing intricate networks [17]. In addition Ln–Cu coordination polymers with idiac give rise to nanoporous material [18], while Zhou et al. reported of an anomalous dielectric behavior and thermal motion of guest water molecules confined in the channels of porous crystals [19]. Iminodiacetate was used also in a polymeric Mn(II) complex showing excellent catalytic activity and

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* Corresponding author. Tel.: +91 3222 276554; fax: +91 3222 275297.
E-mail addresses: sudipta@mail.vidyasagar.ac.in, icsdalai@gmail.com (S. Dalai).

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Three New Co-ordination Polymers of Zinc(II) and Cadmium(II) with Dicarboxylate and Bipyridine Ligands: Synthesis, Structure and Luminescence Study

Debdoot Hazari[1] · **Swapan Kumar Jana**[1] · **Horst Puschmann**[2] · **Ennio Zangrando**[3] · **Sudipta Dalai**[1]

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Abstract Three coordination polymers of zinc(II) and cadmium(II) of formula $\{[Zn(bipy)(NIPH)]_{0.1}\cdot 5H_2O\}_n$ (**1**), $\{[Cd_2(bipy)_2(NIPH)_2]\cdot 2H_2O\}_n$ (**2**) and $\{[Cd_2(bipy)_4(BDAC)(NO_3)](NO_3)\cdot 6H_2O\}_n$ (**3**) (NIPH = 5-nitro-isophthalic acid, H_2BDAC = 1,4-benzenediacrylic acid and bipy = 2,2′-bipyridine) have been synthesized and structurally characterized by X-ray single crystal diffraction analysis. All the complexes display 1D coordination polymers where M(bipy) units are connected by dicarboxylate anions(and also by nitrate in **3**)acting as bridging ligands. While in **1** and **3** a zig–zag chain is generated, in case of **2** a double linear chain is formed by the two crystallographic distinct Cd atoms. In solid state all the complexes expand the dimensionality to 3D by means of π–π interactions among π rings and H-bonds generated by lattice water molecules. The fluorescence study indicates intraligand π–π* charge transfer is the reason for emission in all the complexes.

Keywords Coordination polymer of Zn(II) and Cd(II) · 5-nitroisophthalic acid · 1,4-benzenediacrylic acid · Pi stacking · Luminescence study

1 Introduction

In recent years, the design and construction of metal–organic coordination polymers (MOF) have been at the forefront in the research for new functional materials with applications such as gas adsorption, magnetism, luminescence and catalysis technologies beside their fascinating variety of architectures and topologies [1–3]. In the process of synthesis for such complexes, the key factor is the rational assembly of transition metal ions and organic ligands [4, 5]. Many reports illustrate the use of aromatic dicarboxylic acids acting as organic spacers in the preparation of coordination polymers, [6–8] and the dianionic isophthalate is one of the most common among these ligands [9–11]. In fact dicarboxylate species can bridge metal cations while providing the structural integrity and the required charge balance for the formation of stable neutral crystalline frameworks. In this field 5-nitroisophthalic acid (H_2NIPH) represents a modified organic linker where the electron-withdrawing nitro group could act as possible hydrogen bond acceptor or provide a useful variation affecting the polymer topology, being rather rarely engaged in coordination towards metals as for example in lanthanide networks of 5-nitroisophthalic acid and 1,10-phenanthroline (phen) as ancillary ligand [12]. Nevertheless, in spite of these advantages, the usefulness offered by the 5-nitroisophthalic acid as a possible linker in the assembly of MOFs is still to be exploited in detail [13–15]. Di- or multi-dentate aromatic polycarboxylates have also been used to form robust frameworks since the carboxylate functional groups can exhibit a variety of coordination modes and several groups reported the

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✉ Sudipta Dalai
sudipta@mail.vidyasagar.ac.in; icsdalai@gmail.com

[1] Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapore 721 102, West Bengal, India

[2] Department of Chemistry, Durham University, Darham DH13LE, UK

[3] Department of Chemical and Pharmaceutical Sciences, University of Trieste, 34127 Trieste, Italy

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Three manganese(II) coordination polymers with mixed donor ligands: synthesis, X-ray structures and luminescence properties

Debdoot Hazari[1] · Swapan Kumar Jana[1] · Horst Puschmann[2] · Ennio Zangrando[3] · Sudipta Dalai[1]

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Abstract Three new coordination polymers of manganese(II) of formulae $[Mn_3(phen)_2(phdac)_3]\cdot 2H_2O$ (**1**), $[Mn(4,4'\text{-bipy})(H_2O)_4](cbprop)$(**2**) and $[Mn(2,2'\text{-bipy})(4\text{-nph})(H_2O)_2]_2$ (**3**) (phen = 1,10-phenanthroline, 4,4′-bipy = 4,4′-bipyridine, 2,2′-bipy = 2,2′-bipyridine, H_2phdac = 1,4-phenylenediacetic acid, H_2cbprop = 4-carboxybenzenepropanoic acid and H_2nph = 4-nitrophthalic acid) have been synthesized and structurally characterized by X-ray single-crystal diffraction analysis. The metal complexes possess 2D (**1**), 1D (**2**) and 0D (**3**) dimensionalities. In each case, the crystal packing shows three-dimensional architecture by means of π–π interactions and/or hydrogen bonding supported by coordinated and lattice water molecules. The emission spectra show metal-perturbed intra-ligand π^*–π charge transfer transitions for **1** and π^*–π and π^*–**n** charge transfer transitions for **3**.

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✉ Sudipta Dalai
sudipta@mail.vidyasagar.ac.in; icsdalai@gmail.com

[1] Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapore 721 102, West Bengal, India

[2] Department of Chemistry, Durham University, Durham DH13LE, UK

[3] Department of Chemical and Pharmaceutical Sciences, University of Trieste, 34127 Trieste, Italy

Introduction

Coordination polymers (CPs) of different dimensionalities are among the most flourishing classes of organic–inorganic hybrid functional materials [1–3]. Crystal engineering of CPs has attracted much interest in recent years due to their potential in applications such as catalysis, chirality, conductivity, luminescence, magnetism, spin-transition (spin-crossover), nonlinear optics (NLO) and porosity or zeolitic behavior [4–6]. The chemistry of CPs has advanced considerably in recent years, affording a variety of architectures from various molecular building blocks [7]. However, the rational design of materials with specific crystalline frameworks represents big challenge, because many factors such as metal type, connectivity of organic ligands, solvent, pH and temperature of the reaction have a great influence on the self-assembly process [8–11]. The most commonly used strategies for the synthesis of MOFs are the use of (a) anionic bridging ligands, which may partially or fully counterbalance the charge of the metal centers, (b) suitable anionic or neutral spacers to increase the possibility of enhanced dimensionality of the coordination polymers and (c) the non-coordinating anions.

For the synthesis of CPs with benzene multi-carboxylate ligands, two main strategies have been adopted. The first is the systematic use of benzene multi-carboxylate ligands with various substituent groups on the benzene ring, [12–22], while the second uses a new family of flexible benzene derivatives with long-spanning carboxyl groups [23, 24]. There are several CPs with fascinating topologies formed by semirigid benzene dicarboxylate ligands combining rigid –COOH and flexible $–CH_2COOH$ carboxyl groups, and 1,4-phenylenediacetic acid (H_2pda) and 3-(4-carboxyphenyl)propionic acid are distinctive examples of such flexible ligands. These ligands can adopt various

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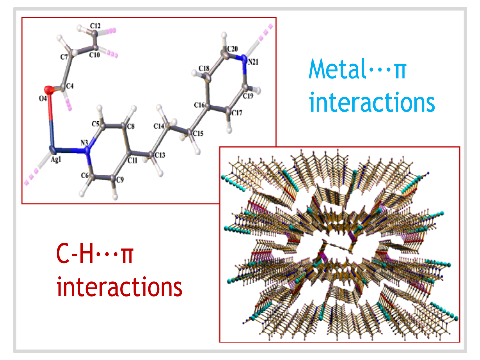
Structural variability of Ag(I) metal–organic networks: C–H···π and metal···π interactions

Debdoot Hazari[a], Swapan K. Jana[a], Saikat K. Seth[b], Horst Puschmann[c] and Sudipta Dalai[a]

[a]Department of Chemistry and Chemical Technology, Vidyasagar University, Midnapore, India; [b]Department of Physics, M. G. Mahavidyalaya, Purba Medinipur, India; [c]Department of Chemistry, Durham University, Durham, UK

ABSTRACT
The synthesis and X-ray structural characterization of two silver(I) coordination polymers, $[Ag_2(bpp)_2(Phdac)]\cdot 5H_2O$ (**1**) and $[Ag_2(bpp)(HSSal)]$ (**2**), are reported, where bpp = 4,4′-trimethylene dipyridine, H_2Phdac = 1,4-phenylenediacetic acid, and H_3SSal = 5-sulfosalicylic acid. X-ray crystallography reveals that the structures are stabilized through hydrogen bonding interactions. The C–H···π and metal···π interactions of aromatic molecules play a crucial role in building a layered framework. Intricate combinations of the weak non-covalent interactions have been analyzed to explore cooperativity and competitiveness in the solid-state structures.



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Silver(I); 1,4-phenylenediacetic acid; 5-sulfosalicylic acid; C–H···π interaction; Metal···π interaction

1. Introduction

Non-covalent interactions are vital in solid and liquid phases [1, 2]. Quantification of these interactions, which manage the molecular aggregation and determine supramolecular assembly, is of fundamental interest [3]. Various non-covalent interactions have attracted attention due to their presence and key role in several fields of science and technology [4]. Besides hydrogen bonds [4], there are other interactions such as those involving aromatic rings, which include cation–π [5], metal cation–π [6], anion–π [7], π–π stacking [8], and CH–π interactions [9].

Interactions formed between a cation and an aromatic ring are of importance in determining the structure and function of supramolecular assemblies of materials science, catalysis, and chemical biology

CONTACT Sudipta Dalai ✉ sudipta@mail.vidyasagar.ac.in

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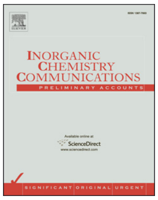

Short communication

1D lead(II) coordination chains with carboxylate containing ligands. A rare example of polyrotaxane 1D → 1D interpenetrated coordination polymer

Debdoot Hazari [a], Swapan Kumar Jana [a], Horst Puschmann [b], Ennio Zangrando [c,*], Sudipta Dalai [a,*]

[a] Department of Chemistry and Chemical Technology,Vidyasagar University, Midnapore 721 102, West Bengal, India
[b] Department of Chemistry, University of Durham, Durham DH13LE, UK
[c] Department of Chemical and Pharmaceutical Sciences, University of Trieste, 34127 Trieste, Italy

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ABSTRACT

The structural determination of two interesting lead(II) coordination polymers, namely $[Pb(ind)_2(H_2O)]_n$ (**1**) and $[Pb_2(dbsf)_2(bipy)]_n$ (**2**) (Hind = indane-2-carboxylic acid, H_2dbsf = 4,4′-sulfonyldibenzoic acid, and bipy 4,4′-bipyridine), reveals in the second an unexpected polyrotaxane 1D → 1D interpenetrated coordination polymer thanks to the hemidirected coordination geometry of the metal and the rings formed by the dicarboxybiphenyl sulfone ligands along the 1D chain.

In recent years different levels of interpenetration have been reported and such assemblies most commonly involve interpenetrated 2D or 3D frameworks [1], while interpenetrated 1D polymers are rather rare since these polymers require the presence of rings in the chain [2]. In addition a literature survey shows that most of metal–organic framework (MOF) research is focused on complexes comprising transition metals due to their unique structures and potential applications, while MOFs containing main group metals are less explored. Recently, the rapid development of materials science and crystal engineering moved the interest of inorganic chemists towards the investigation of Pb(II) complexes. The attention was dictated also by the presence in this metal of the 6s electron lone pair that drives the coordination sphere towards unusual geometries. In fact the stereochemically active 6s electrons usually give rise to a hemidirected coordination geometry leaving a distinct void or gap in the coordination sphere; on the contrary the lack of this void is indicative of stereochemically inactive 6s lone pair [3–5]. Continuing our interest in the use of lead(II) in the construction of polymeric complexes [5], we report herein the synthesis, structural determination of two new Pb compounds $[Pb(ind)_2(H_2O)]_n$ (**1**) and $[Pb_2(dbsf)_2(bipy)]_n$ (**2**), built by carboxylate containing ligands (Hind = indane-2-carboxylic acid, H_2dbsf = 4,4′-sulfonyldibenzoic acid, and bipy 4,4′-bipyridine).

The two compounds have been synthesized from $Pb(NO_3)_2$ and indane-2,2′-dicarboxylic acid in aqueous solution, the second by adding 4,4′-sulfonyldibenzoic acid to an aqueous solution of 4,4′-bipyridine and $Pb(OAc)_2.3H_2O$. In both cases colorless needle and block shaped crystals, respectively, were isolated after few days at room temperature.

The single crystal X-ray diffraction analysis of compound **1** [6], of formulation $[Pb(ind)_2(H_2O)]$n, revealed that it crystallizes in monoclinic space group $P\,2_1$, and the asymmetric unit consists of the metal ion, two indane-2-carboxylate, one water molecule. The complex is a 1-D chain-like coordination polymer with lead atom chelated by two indan-2-carboxylato groups and by two oxygens, which come from symmetry related different ind ligands. The coordination sphere is completed by a water molecule (Fig. 1). In the PbO_7 chromophore the Pb–O(carboxylate) bond distances range from 2.503(13) to 2.662(13) Å, while the Pb–OH_2 bond is slightly longer of 2.745(7) Å. The coordination environment around Pb shows an evident void [the largest bond angles are O(3)–Pb–O(1w) = 150.2(4)°, O(4)–Pb–O(2″) = 143.2(4)°] with all the Pb–O bonds distributed in a hemisphere. The structural consequence is a hemidirected coordination geometry of the Pb center due to the presence of the stereochemical active 6s lone pair electrons. In the coordination sphere the chelating carboxylate groups form a dihedral angle of 88.5°.

Of the two crystallographic independent carboxylate groups, one is chelating (O3/O4), while the other (O1/O2) acts as chelating–bridging (μ-η^1:η^2:η^1) connecting three Pb atoms giving rise to a 1D polymer elongated along axis *b* (Fig. 2). The intermetallic distance is of 4.291(1) Å and a Pb…Pb…Pb angle of 112.79(1)°. It is worth noting that the chain is reinforced by intramolecular H-bonds between O1w and carboxylate group O3/O4 (O1w…O3 = 3.14(3) Å, O1w–H1a…O3 = 164°; O1w…O4 = 2.60(2) Å, O1w–H1b…O4 = 175°), and the

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[*] Corresponding authors.
E-mail addresses: ezangrando@units.it (E. Zangrando), sudipta@mail.vidyasagar.ac.in (S. Dalai).

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Title: One-Dimensional Zinc-Based Coordination Polymer as a Higher Capacity Anode Material for Lithium Ion Batteries

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Date: Oct 1, 2017

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Title: {[Hg(SCN)3]2(μ-L)}2−: An Efficient Secondary Building Unit for the Synthesis of 2D Iron(II) Spin-Crossover Coordination Polymers

Author: Daopeng Zhang, Francisco Javier Valverde-Muñoz, Carlos Bartual-Murgui, et al

Publication: Inorganic Chemistry

Publisher: American Chemical Society

Date: Feb 1, 2018

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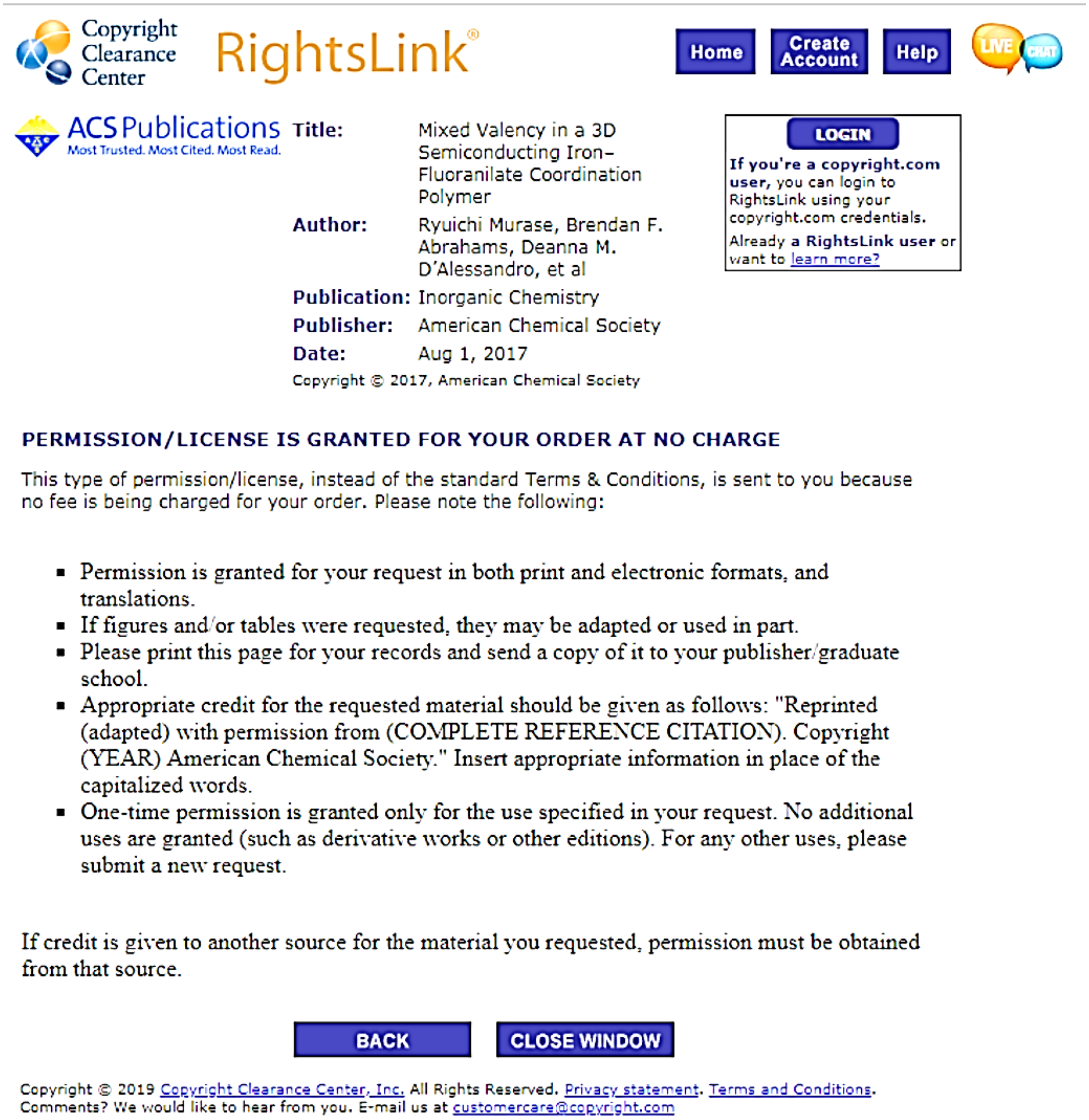

Title:	Mixed Valency in a 3D Semiconducting Iron–Fluoranilate Coordination Polymer
Author:	Ryuichi Murase, Brendan F. Abrahams, Deanna M. D'Alessandro, et al
Publication:	Inorganic Chemistry
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