Battlement-shaped 1D coordination polymer based on a bis(N-methylimidazole-2-yl)butadiyne ligand
Battlement-shaped 1D coordination polymer based on a bis(N-methylimidazole-2-yl)butadiyne ligand†

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Bis(N-methylimidazole-2-yl)butadiyne (bmib) has been prepared starting from N-methylimidazole following two different pathways. Bmib fluoresces and is capable of forming 1D coordination polymers by clamping together metal units. The molecular structure of a zinc coordination polymer based on bmib and zinc acetate resembles a battlement of a fortress.

Unsaturated organic ligands in combination with transition metals can be used as precursors for inorganic–organic materials. These materials, based on their architecture and characteristics, are of great interest regarding catalysis, nonlinear optics, or properties that may be useful in electronic applications or as molecular sensors.1 Molecular nonlinear optics, or characteristics, are of great interest regarding catalysis, materials. These materials, based on their architecture and starting from N-methylimidazole (1) (Scheme 1).8 A Wittig reaction of 2-iodo-1-methylimidazole resulted in 2-(2′-chlorovinyl)-N-methylimidazolide that was obtained as a 2:1 mixture of E/Z isomers 3a/b. Treating 2-(2′-chlorovinyl)-N-methylimidazolide (3a/b) with potassium tert-butoxide yielded the 2-ethyl-N-methylimidazolide (6) suitable for a Glaser coupling. Due to a rather cumbersome purification of 3a/b, mostly caused by unreacted Wittig reagent, we decided to follow another route to 2-ethyl-N-methylimidazolide (6). This second approach involved 2-iodo-1-methylimidazolide (4) which is gained by a reaction of 1-methylimidazolide (1) with n-butyl lithium and I2.9 The resulting imidazolide 4 was treated under Sonogashira coupling conditions to yield 2-trimethylsilylvinyl-1-methylimidazolide (5).10 After desilylation with KF, bis(N-methylimidazolide-2-yl)butadiyne (bmib) (7) was obtained by a homocoupling Glaser reaction of 6 catalyzed by CuCl in pyridine (Scheme 1).

Bmib (7) crystallizes in the space group P21/c, and the result of an X-ray single crystal structure determination shows the presence of intermolecular π-stacking (Fig. 1). The average distance between the centres of the stacking imidazolides is approximately 3.6–3.7 Å. Bond distances of the acetylene chain show prevalent values with an energetic spacing of 2000 cm−1. These are assigned to the triple bond centered π* excited state. Following excitation at a wavelength of 300 nm, an emission spectrum that gives

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rise to a 115 nm red-shifted maximum at 415 nm evolves. Emission quantum yields were as high as $1.5 \times 10^{-3}$ and $1.1 \times 10^{-3}$ in CHCl$_3$ and THF, respectively.

Further insights into the excited state deactivation of bmib (7) came from transient absorption measurements following femtosecond and nanosecond excitation in THF (Fig. 3, top). Upon 258 nm excitation, we note intense transient absorption features throughout the visible and near-infrared region, which maximize at 490, 555, and 939 nm. We interpret these differential absorption changes as the population of the singlet excited state of bmib (7). On a rather short timescale,
that is, 25 ± 5 ps, these transient absorption features decay. At the end of this decay, we note a broad transient absorption throughout the visible and near-infrared region with maxima at 450 and around 1100 nm. The latter are stable and are still discernible at the end of the experimental timescale of 7.5 ns. Tentatively, we ascribe these transients to the triplet excited state of bmib (7). To explore the triplet excited state deactivation, nanosecond transient absorption measurements with 266 nm laser pulses were performed (Fig. 3, bottom). The nanosecond transient absorption spectrum is in perfect agreement with what was observed at the end of our femtosecond transient absorption measurements. In particular, transient absorption features with maxima at 450 and around 1100 nm were noted. A kinetic analysis revealed two lifetimes—a short-lived component with 1.7 ± 0.2 and a long-lived component with 7.9 ± 0.5 μs. The two components are likely to arise from triplet–triplet annihilation and ground-state quenching. Support for the assignment that the transient features correlate with the triplet excited state of bmib (7) came from analogous experiments in oxygen-saturated solutions. In the latter, the triplet excited lifetime is reduced to 80 ± 5 ns.

Reaction of bmib with Zn(OAc)₂ yielded a 1D polymeric compound. The X-ray structure analysis revealed coordination polymer [Zn₃(OAc)₁₀(bmib)]ₙ, consisting of alternating dinuclear [Zn₂(O₂CCH₃)₆] paddle-wheel units and trinuclear [Zn₃(O₂CCH₃)₆] units “clamped” together by bmib ligands. This rather unusual coordination mode of the bmib ligand causes a one-dimensional sequence that resembles a battlement of a fortress (Fig. 4). Zinc acetate is capable of forming coordination polymers with N,N-donor ligands by either having a paddle-wheel or trinuclear inorganic unit.¹³⁻¹⁶ To the best of our knowledge, such alternating paddle-wheel and trinuclear units have been reported only once in literature before.¹⁹

The trinuclear Zn(n) acetate unit is constructed by six bridging acetate ligands and similar to previously described trinuclear zinc carboxylates with axial N- or O-donor ligands.¹³⁻¹⁶ There is an inversion centre on the central Zn atom. Out of three Zn atoms, the central Zn is all O-donor hexacoordinated from six acetate groups to form a distorted octahedron. The two terminal Zn centres are coordinated tetrahedrally by three oxygen atoms of the acetate groups and by the nitrogen atom of the bmib ligand. Two different types of carboxylate coordination were found in this unit. Four acetate ligands show κ²-coordination, forming syn–syn bridges between central and terminal zinc ions. The other two acetate ligands are κ¹-coordinated and function as Zn–O–Zn μ-bridges with one uncoordinated oxygen atom slightly involved in a weak interaction with the zinc atom (d(Zn3⋯O32) = 2.645(4) Å).¹⁷ The paddle-wheel unit is constructed by two symmetrically equivalent Zn atoms, which are μ-bridged by four acetate ligands. Each Zn atom in this unit is in a distorted square pyramidal environment, with four oxygen atoms from acetates, to form the equatorial plane, and one nitrogen atom of the bmib ligand. In the paddle-wheel unit, the Zn–O bond distances range from 2.035(3) to 2.077(4) Å and the Zn–N bond distance amounts to 2.034(4), which compare well to values of related compounds.¹³,¹⁸ In the trinuclear unit, the Zn–O bond distances of the κ²-OAc range from 1.938(4) to 2.118(3) Å. The κ¹-OAc shows a bond distance of 2.129(3) for Zn1–O31 and 1.980(3) for Zn3–O31. The Zn–N bond distance of 2.002(4) Å is slightly shorter than in the dinuclear unit. The Zn–Zn distances of dinuclear and trinuclear units are 2.9489(10) and 3.3287(6) Å, which are similar to literature values.²⁰ The bond distances of the bmib ligand do not vary significantly from those of the free ligand. It is worthwhile mentioning that obviously bmib (7) acts as some sort of molecular clip for metal ions with almost fixed angles ∠(M–N₁₁–N₂₁) close to 90° and torsion angles ∠(M–N₁₁–N₂₁–M’) close to 0°. A similar coordination property has recently been reported for the slightly shorter 1,4-bis(N-methylimidazole-2-yl)benzene ligand.²⁰

Conclusion

The ligand 1,4-bis(N-methylimidazole-2-yl)butadiyne (bmib) (7) shows fluorescent properties in solution and intermolecular π-stacking in the crystal structure. Bmib (7) possesses remarkable coordination properties, as is indicated by the formation of a coordination polymer [Zn₃(OAc)₁₀(bmib)]ₙ (8). The X-ray diffraction revealed an interesting battlement-type structure.
with alternating trinuclear and dinuclear paddle-wheel zinc acetate units clamped together by bmib (7). The metal–bmib–metal units resemble the geometry of retaining clips.

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Notes and references