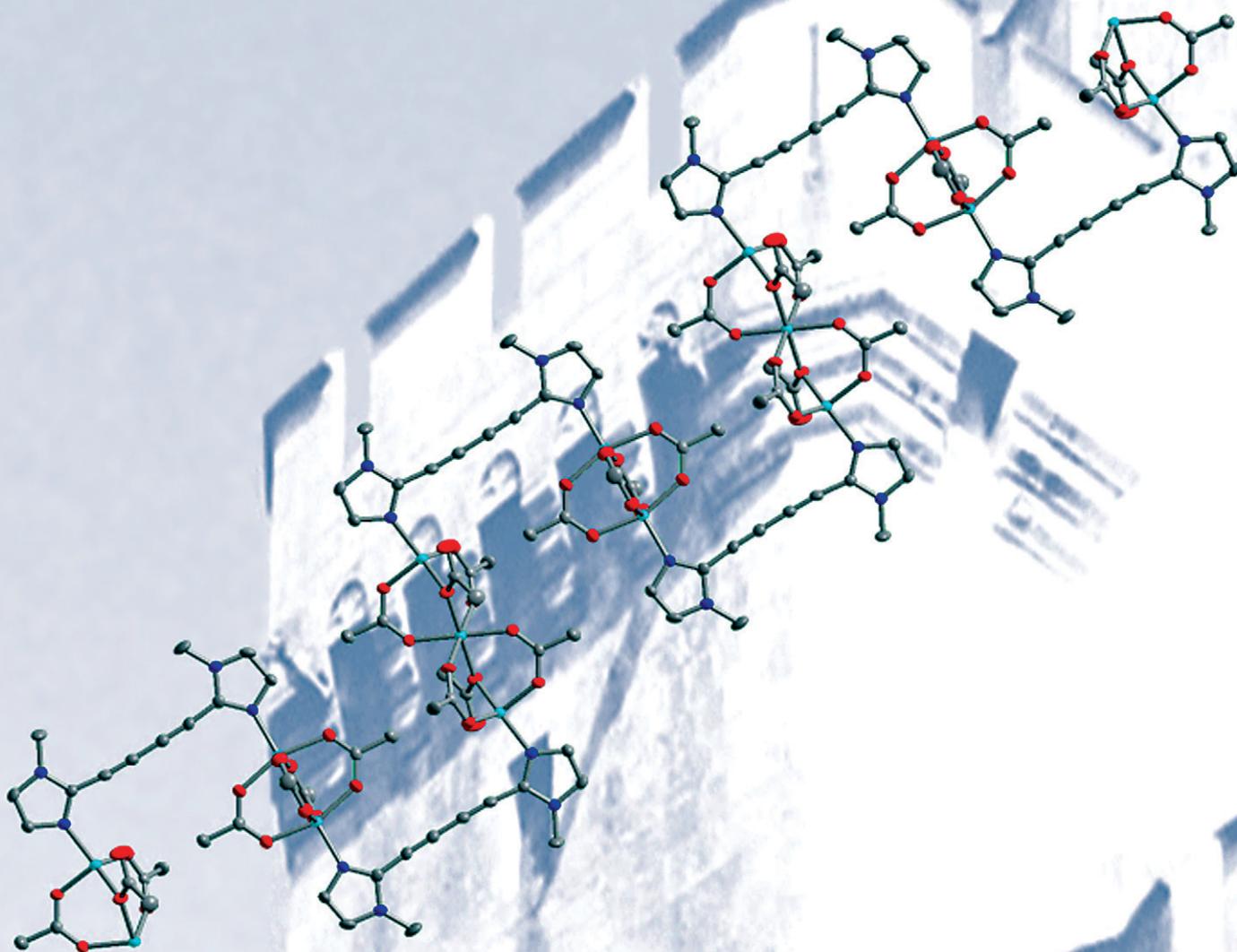


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**COVER ARTICLE**

Guldi, Burzloff *et al.*  
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bis(*N*-methylimidazole-2-yl)butadiyne ligand

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

Thomas Waidmann,<sup>a</sup> Nico Fritsch,<sup>a</sup> Johannes Tucher,<sup>a</sup> Marc Rudolf,<sup>b</sup> Felix Glaser,<sup>a</sup> Dirk M. Guldi<sup>\*b</sup> and Nicolai Burzlaff<sup>\*a</sup>

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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.<sup>1</sup> Molecular self-assembly is at the heart of crystal engineering and is based on complementary and explicit interactions between the components in order to generate the final product.<sup>2</sup> Two new branches excelled in this still emerging field, namely metal–organic coordination networks (MOCNs) or metal–organic frameworks (MOFs) and supramolecular coordination complexes (SSCs).<sup>3</sup> Synthesis of highly ordered coordination polymers can lead to molecular networks with different dimensions, *e.g.* linear polymers or “zigzag” chains and 2D planar or 3D polymer networks.<sup>1–4</sup> Our special interest focuses on the synthesis of new appropriate organic *N,N*-ligands suitable for 1D coordination polymers.<sup>2a,b,5</sup> In recent years, polyne-bridged heterocycles, such as bis(4-pyridyl)butadiyne, have been proven to be powerful ligands for chain and

square-grid architectures.<sup>6</sup> Recently, we reported on *trans*-1,2-bis(*N*-methylimidazole-2-yl)ethylene (*trans*-bie) which turned out to be a versatile building block for 2D and especially 1D coordination polymers.<sup>7</sup> Inspired by the results gained, we decided to aim for the new linear bis(*N*-methylimidazole-2-yl)butadiyne (bmib) (7).

The first approach to get hands on the bmib ligand started with 1-methylimidazole-2-carbaldehyde (2) that is accessible from 1-methylimidazole (1) (Scheme 1).<sup>8</sup> A Wittig reaction of 2 and chloromethylene-(triphenyl)phosphine resulted in 2-(2'-chlorovinyl)-*N*-methylimidazole that was obtained as a 2:1 mixture of *E/Z* isomers 3a/b. Treating 2-(2'-chlorovinyl)-*N*-methylimidazole (3a/b) with potassium *tert*-butoxide yielded the 2-ethynyl-*N*-methylimidazole (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-ethynyl-*N*-methylimidazole (6). This second approach involved 2-iodo-1-methylimidazole (4) which is gained by a reaction of 1-methylimidazole (1) with *n*-butyl lithium and I<sub>2</sub>.<sup>9</sup> The resulting imidazole 4 was treated under Sonogashira coupling conditions to yield 2-trimethylsilyl ethynyl-1-methylimidazole (5).<sup>10</sup> After desilylation with KF, bis(*N*-methylimidazole-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 *P*2<sub>1</sub>/*c*, and the result of an X-ray single crystal structure determination shows the presence of intermolecular  $\pi$ -stacking (Fig. 1). The average distance between the centres of the stacking imidazoles is approximately 3.6–3.7 Å. Bond distances of the acetylene chain show prevalent values with a triple bond distance of 1.202 Å.<sup>6a,11</sup>

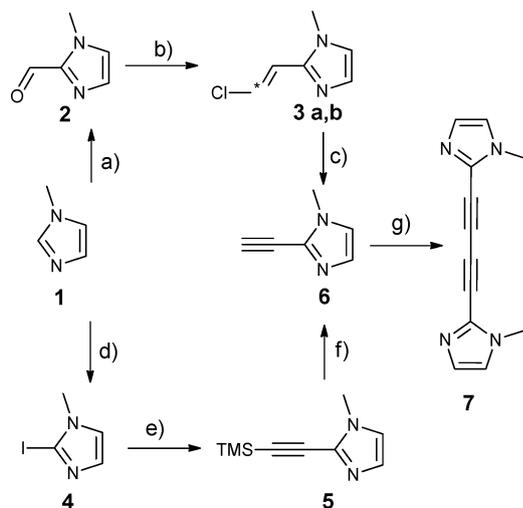
Similar to related compounds,<sup>12</sup> the absorption spectrum (Fig. 2) of bmib (7) gives rise to vibronic transitions in the 280 to 350 nm range with maxima at 292, 308, 328, and 350 nm with an energetic spacing of 2000 cm<sup>-1</sup>. These are assigned to the triple bond centered  $\pi$ - $\pi^*$  excited state. Following excitation at a wavelength of 300 nm, an emission spectrum that gives

<sup>a</sup> Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany. E-mail: nicolai.burzlaff@fau.de; Fax: +49 9131 85 27387; Tel: +49 9131 85 28976

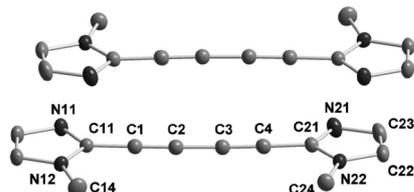
<sup>b</sup> Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany. E-mail: dirk.guldi@fau.de; Fax: +49 9131 85 27341; Tel: +49 9131 85 28307

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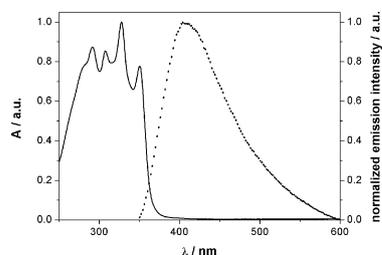




**Scheme 1** Synthesis of bmib *via* two different pathways. (a) *n*-BuLi, DMF, THF. (b) *n*-BuLi, (chloromethyl)triphenylphosphonium chloride, THF. (c) KO<sup>t</sup>Bu, NH<sub>4</sub>Cl, THF. (d) *n*-BuLi, I<sub>2</sub>, THF. (e) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, Et<sub>3</sub>N, DMF, TMS-acetylene. (f) KF, MeOH. (g) CuCl, O<sub>2</sub>, pyridine.



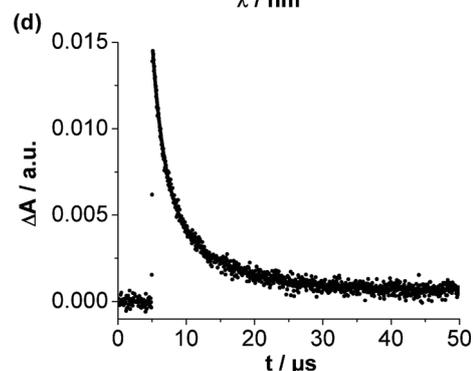
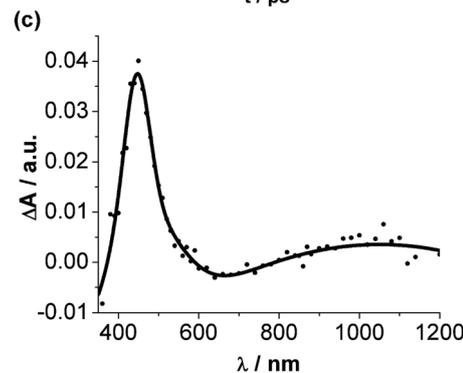
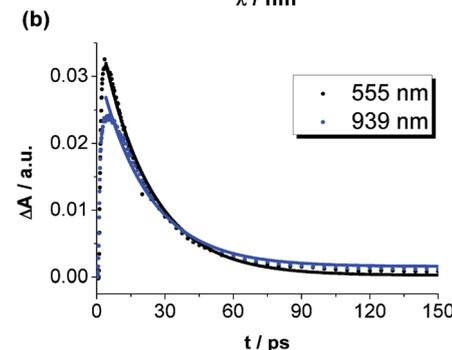
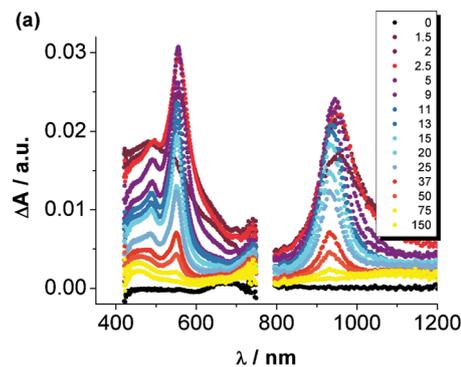
**Fig. 1** The molecular structure of bmib (**7**); thermal ellipsoids are drawn at the 30% probability level, and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): C3–C2, 1.366(19); C2–C1, 1.202(19); C1–C11, 1.417(18); C14–N12, 1.454(17); C2–C1–C11, 179.05(14); C3–C2–C1, 178.35(14); N11–C11–C21–N21, 178.04(14).



**Fig. 2** The absorption (solid line) and emission (dotted line) spectra for bmib (**7**) in CHCl<sub>3</sub> at 300 nm excitation wavelength.

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<sub>3</sub> 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



**Fig. 3** (a) Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump-probe experiments (258 nm) of bmib (**7**) in argon-saturated THF with several time delays between 0 and 150 ps at room temperature. (b) Time-absorption profiles of the spectra shown in (a) at 555 and 939 nm, monitoring the intersystem crossing. (c) Differential absorption spectra (visible and near-infrared) obtained upon nanosecond flash photolysis (266 nm) of bmib (**7**) in argon-saturated THF at 50 ns after excitation at room temperature. (d) Time-absorption profile of the spectrum shown in (c) at 450 nm, monitoring the excited state decay.

differential absorption changes as the population of the singlet excited state of bmib (**7**). On a rather short timescale,





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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