AZOBENZENE-BASED METALLOHELICATES: SYNTHESIS, SELF-ASSEMBLY AND PHOTOISOMERISATION STUDIES

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Azobenzene derivatives are widely investigated because of their reversible *trans–cis* photoisomerisation and their potential for incorporation into responsive molecular architectures.[1] Integrating azobenzene units into metal-directed supramolecular systems offers a strategy to combine photo-switchable organic chromophores with well-defined coordination assemblies. In this work, we report the synthesis and characterisation of a new bis-bidentate iminopyridine ligand bearing two azobenzene units, together with its self-assembly into binuclear triple-stranded helicates with Zn(II) and Fe(II).

The ligand was obtained through a four-step synthetic route designed to provide sufficient solubility and stability for coordination studies. Self-assembly with Zn(II) and Fe(II) tetrafluoroborate salts in CH_2Cl_2/CH_3CN mixtures afforded the corresponding metallohelicates $[M_2(L)_3](BF_4)_4$ (M = Zn(II), Fe(II)) (Fig. 1). UV–Vis titration experiments were carried out to investigate the complex formation and determine the ligand-to-metal stoichiometry.

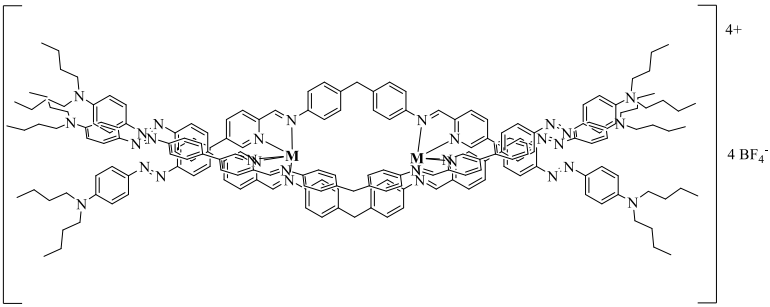

Fig. 1. Chemical structure of the azobenzene-functionalized triple-stranded helicate with M = Zn(II) or Fe(II)

The formation of the supramolecular helicates was confirmed by high-resolution electrospray ionisation mass spectrometry (HR-ESI-MS). Diffusion-ordered spectroscopy (^{1}H DOSY NMR) was further employed to evaluate the size of the assemblies in solution, revealing a significant increase in hydrodynamic radius upon coordination, consistent with the formation of larger supramolecular structures.

The photophysical properties of the ligand and its complexes were investigated by UV–Vis spectroscopy in solution. In addition, time-resolved UV–Vis spectroscopy was used to study the photoisomerisation behaviour of the azobenzene-containing ligand and to monitor the light-induced *trans–cis* interconversion and the corresponding relaxation processes.

Finally, density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed to analyse the electronic structure of the ligand and to support the interpretation of the experimental absorption spectra.

1. M. Baroncini, J. Groppi, S. Corra, S. Silvi and A. Credi, *Adv. Opt. Mater.*, 2019, **7**, 1900392.