



Thiophene/furan units decorated unsymmetrical dinuclear metallocalix[4]arenes

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ABSTRACT

Twelve new dinuclear metallocalix[4]arenes (**1–12**) decorated with two thiophene units/two furan units were synthesized using a newly designed flexible ditopic nitrogen donors, a bis-chelating ligands, and $\text{Re}_2(\text{CO})_{10}$ and were structurally characterized by various spectroscopic methods. The structures of **1**, **5** and **9** were confirmed by single crystal X-ray diffraction analysis. The photophysical properties of the ligands were studied. The structures of **1**, **3** and **5–12** were optimized using DFT-calculations.

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Introduction

The interest in designing various shapes and sizes of supramolecular coordination complexes (SCCs) with different functionality is increasing continuously due to their potential applications in materials and medicinal fields [1–18]. Among the many types of SCCs, the *fac*- $\text{Re}(\text{CO})_3$ -core based SCC's are one of the types which attracted in host-guest chemistry, catalysis, probes for photoluminescence quenching, anticancer agents and photo- and electro-chemical sensors [17–33]. The rhenium SCC's can be assembled using either rigid pyridine-based donors or flexible benzimidazolyl based donors with/without anionic ancillary ligands [17–33]. Recently, the flexible benzimidazolyl based donor ligands are getting attention owing to their easy synthetic preparation, and easy to introduce functionality either on the benzimidazolyl moiety or spacer unit [32–41]. In addition, the flexible ligands offer curved framework to assemble the rhenium based metallocalixarenes/metallocavitands [39–41]. The uniqueness about the metallocalix[4]arenes is that these complexes adopt cone shaped structure and possess solvent accessible cavity, which are important for further potential applications. We have earlier

reported dinuclear, heteroleptic neutral metallocalix[4]arenes with/without aliphatic decorated units on a wall [41]. As a continuation of our work on this field, we predict that introducing a five-membered materially and biologically useful heterocyclic units on the benzimidazolyl unit of flexible ligand would result in new types of metallocalix[4]arenes possessing new properties. Herein, four new thiophene/furan (L^1 – L^4 , Fig. 1) bearing ditopic benzimidazolyl based donors were designed, synthesized and successfully used as a building block for assembling a series of metallocalix[4]arenes (**1–12**) bearing different decorating functional units. The ligands and metallo macrocycles were characterized by elemental analysis, FT-IR, and ^1H NMR spectroscopic methods. The metallocavitands **1**, **5** and **9** were further characterized by single crystal X-ray diffraction method.

Results and discussion

Synthesis and characterization of functional ligands

The ligands (L^1 – L^4 (Fig. 1)) were synthesized by treating 2-thiophene-1*H*-benzimidazole/2-furan-1*H*-benzimidazole with 1,4-di(bromomethyl)benzene/1,4-di(bromomethyl)-2,5-dimethoxybenzene in the presence of strong base (KOH) in DMF at room temperature following the synthetic approach used to obtain the unsubstituted flexible di/tri/tetraptopic benzimidazolyl donors [38] (Scheme 1). All the ligands are air- and moisture stable and are soluble in polar organic solvents. The ^1H NMR spectrum of L^1 shows

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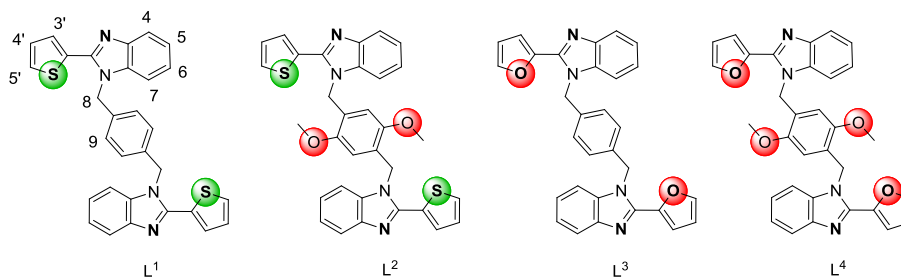
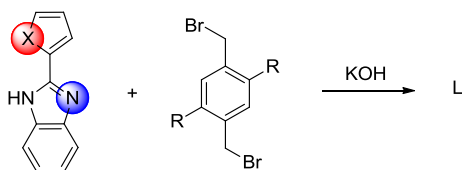


Fig. 1. Furan/thiophene units substituted ditopic ligands, L¹–L⁴.



Scheme 1. Synthesis of ligands L¹–L⁴.

well-resolved peaks for all the protons (Fig. 2). The proton ratio of 2-thiophenebenzimidazolyl- and *p*-xylene-units is 2:1, confirming the stoichiometry of the ligand. Compared to the free 2-thiophene-1H-benzimidazole, the protons in L¹ were shifted upfield and downfield. The disappearance of the NH proton peak at 13 ppm, and the appearance of two singlets at 7.0 (*p*-phenylene) and 5.7 (methylene) ppm indicate the formation of ligand L¹. The ¹H NMR spectra of L²–L⁴ also show the similar pattern to that of the ligand L¹ (Fig. S1–S4).

Synthesis and characterization of metallocavitands 1–12

The metallocavitands 1–12 were synthesized by treating equimolar amounts of Re₂(CO)₁₀, bis-chelating units (H₂-dhnq/H₂-THBQ/H₂-CA) and nitrogen donors (L) in mesitylene/toluene by one-step process [41] (Scheme 2). The products 1–12 are air and moisture stable, and are soluble in acetone, acetonitrile and DMSO. The FT-IR spectra of complexes show characteristic peaks for the *fac*-Re(CO)₃-unit in the region 1800–2200 cm⁻¹. The ¹H NMR spectrum of 1 show well resolved peaks for the protons of L¹- and dhnq²⁻ units with 1:1 ratio (Fig. 3). There is no difference found in the position and pattern of chemical resonances of protons of L¹ in complex 1 and free ligand L¹. However, the formation of metallocycle is evident from the appearance of the two multiplets (H^a and H^b) with equal intensity for the coordinated i.e. bis-chelated

dhnq²⁻ unit; the free H₂-dhnq does not show any chemical resonance in d₆-DMSO at 25 °C due to the poor solubility. To confirm further, the mixture of (L¹ + Ag⁺), and (1 + Ag⁺) were studied by ¹H NMR spectroscopy and compared with complex 1 (Fig. 4). The ¹H NMR pattern of all three systems are different from each other. This indicates that L¹ remains in the cyclic framework of the metallocycle. Complexes 2–4 also show similar spectral pattern like that of metallocycle 1.

The marked chemical shift difference was found for the protons of N-donors (L¹) in the complex 5. The ¹H NMR spectrum of 5 show two sets of peaks with 1:0.5 intensity ratio for L¹ unit (Fig. 5). One set of peaks do not change their position in relative to that of the free L¹, whereas the other set of peaks were shifted downfield and upfield. The appearance of singlet with upfield shift for *p*-phenylene unit in 5 compared to L¹, indicates that all four protons in the *p*-phenylene experience a ring-current effect. The proton signals of methylene group split into two sets of doublets with coupling constants consistent with geminal coupling (16 Hz). In addition, the proton peaks appeared at 6.74 ppm and 2.19 ppm suggesting the presence of mesitylene solvent molecules. However, the same sample of 5 was recorded after eight days and show a single set of peaks for all protons with no significant shift in their position in relative to free L¹ ligand (Fig. 5). This may be due to the minor isomer of 5 gradually converted into major isomer of metallomacrocycle 5. Similarly, no significant difference found between the free ligands and the complexes 6–12 (Fig. S5–S16).

Crystal structures of 1, 5 and 9

A single-crystal X-ray diffraction analysis of metallomacrocycles 1, 5 and 9 show that the complexes adopt a M₂LL'-type architecture, which is made up of two *fac*-Re(CO)₃-cores, one bis-chelating unit

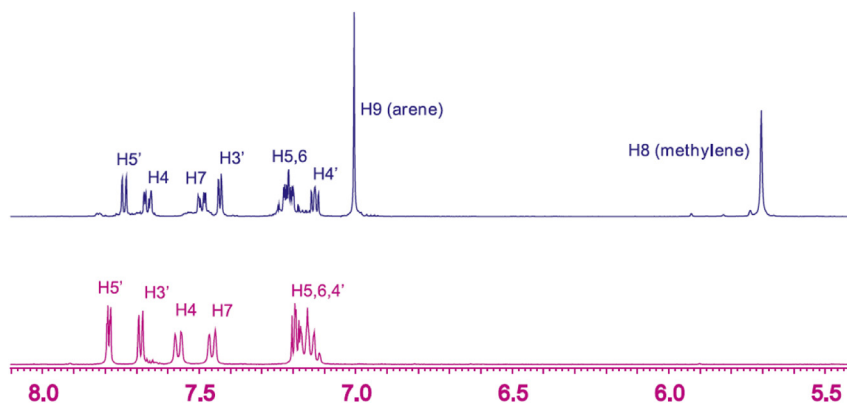


Fig. 2. ¹H NMR spectra of 2-thiophene-1H-benzimidazole (bottom) and ligand L¹ (top) in DMSO-d₆.

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