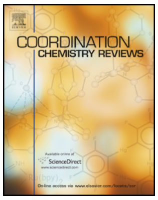
Coordination Chemistry Reviews 280 (2014) 96–175

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Neutral discrete metal–organic cyclic architectures: Opportunities for structural features and properties in confined spaces

Pounraj Thanasekaran, Cheng-Hua Lee, Kuang-Lieh Lu*

Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan

Contents

ARTICLE INFO

Article history:
Received 11 April 2014
Accepted 14 July 2014
Available online 10 August 2014

ABSTRACT

An emerging class of neutral metal–organic supramolecules has led to some fascinating and sophisticated structures including their photophysics and host–guest properties that have attracted the imagination of chemists. Synthetic routes including step-wise and one-step strategies have been employed to achieve the targeting of neutral structures. Several discrete neutral assemblies of various nuclearities, in which the coordination geometries for transition metals include octahedral, tetrahedral, and square planar, integrating main-group elements in supramolecular self-assembly applications allows for the formation of markedly different structural motifs. The structural characteristics of the ligands as well as the metal centers present in the neutral metallacycles allow easy tuning of their emission properties. Therefore,

---

Abbreviations: azpy, 4,4′-*trans*-azopyridine; apyz, aminopyrazine; 2,2′-bpdc^{2-}, 2,2′-biphenyldicarboxylate; bpe, *trans*-1,2-bis(4-pyridyl)ethylene; bpp, 1,4-bis(4-pyridyl)piperazine; btp, 1,3-bis(1,2,4-triazol-1-yl)propane; BiBzIm, 2,2′-bisbenzimidizolate; benzbix, α,α′-bis(benzimidazole-1-yl)-*para*-xylene; bix, α,α′-bis(imidazole-1-yl)-*para*-xylene; bpym or bpm, 2,2′-bipyrimidine; 2-BPT, 3,5-bis(2-pyridyl)-1,2,4-triazole; bipy or bpy, 4,4′-bipyridine; CD, circular dichroism; COD, cyclooctadiene; 1,4-chdc^{2-}, 1,4-cyclohexanedicarboxylic acid; CT, charge transfer; dabco, 1,4-diazabicyclo[2.2.2]octane; dpa, dipyridylamine; DAniF, *N*,*N*′-di(*p*-anisyl)formamidinate; DPhF, diphenylformamidinate; dmGly, *N*,*N*-dimethylglycine; 3′-*cis*-DPyP, 5,10-bis(3′-pyridyl)-15,20-diphenylporphyrin; 4′-*trans*-DPyP, 5,15-bis(4′-pyridyl)-10,20-diphenylporphyrin; 4′-*trans*DPyP-npm, 5,15-bis(4′-pyridyl)-2,8,12,18-tetra-*n*-propyl-3,7,13,17-tetramethylporphyrin; dmso, dimethylsulfoxide; dmpz, 3,5-dimethylpyrazolate; dpa, dipyridylamine; dppf, 1,1′-bis(diphenylphosphanyl)ferrocene; dppm, 1,1-bis(diphenylphosphino)methane; dps, 4,4′-dipyridyl sulfide; EpBim, 2-(4-pyridyl)-1-ethyl-benzimidazole; 1,4-chdc^{2-}, *cis*- and *trans*-1,4-cyclohexanedicarboxylate; HBim-C_5H_3N, α,α′-bis(benzimidazol-1-yl)-*o*-xylene; HPNP, 2-(hydroxypropyl)-*p*-nitrophenyl phosphate; Hpyz^{Ph}, 2,5-dihydro-3-methyl-5-oxo-1-*phenyl*-pyrazole-1-carbothiamide; HpzAnMe, 2-(pyrazolyl)-4-toluidine; H_2bbim, 2,2′-bis(benzimidazole); H_2DBImB, 1,4-di(benzimidazolyl)benzene; H_2CA, chloranilic acid; H_2dhaq, 1,4-dihydroxy-9,10-anthraquinone; H_2DBImB, 1,4-di(benzimidazolyl)benzene; H_2dhnq, 5,8-dihydroxy-1,4-naphthoquinone; H_2[ONNO], 1,4-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)piperazidine; H_2thaq, 1,2,4-trishydroxy-9,10-anthraquinone; H_4aahz, *N*-acetylaminobenzhydrazide; H-fmt, 2-furanmethanethiol; hmt, hexamethylenetetramine; H_2tbip, 5-*tert*-butyl isophthalic acid; *m*-H_3tpat, 2,4,6-tris(3-picolylamino)-1,3,5-triazine; H_2thaq, 1,2,4-trishydroxy-9,10-anthraquinone; H_2XyTs, *N*,*N*′-bis(2-tosylaminobenzylidene)-1,4-xylylenediamine; Im, imidazole; 3-imntd, *N*,*N*′-bis(3-imidazol-1-yl propyl)naphthalenediimide; MLCT, metal-to-ligand charge transfer; Nbenzbix, 1,4-bis(2-nonylbenzimidazol-1-ylmethyl)benzene; LC, ligand-centered; LLCT, ligand-to-ligand charge transfer; LMCT, ligand-to-metal charge transfer; LMLCT, ligand-to-metal-to-ligand charge-transfer; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; *p*-NBimM, 1,4-bis(5,6-dimethylbenzimidazol-1-ylmethyl)-naphthalene; PAH, pyromellitic dianhydride; phen, 1,10-phenanthroline; phba, 4-hydroxybenzoate; psb, 1,4-bis(dimethyl-4-pyridylsilyl)benzene; 4-PyS, pyridine-4-thiolate; PyDTM, pyrrolidinedithioester; Pro, ʟ-proline; py, pyridine; pz, pyrazine; TBPhe^{2-}, *N*,*N*′-terephthaloyl-bis(*L*-phenylalaninato); TDDFT, time-dependent density functional theory; tht, tetrahydrothiophene; terpy, 2,2′:6′,2″-terpyridyl; thq, tetrahydroxy-1,4-quinone; tpbb, 2,5-bis(5-*tert*-butyl-2-benzoxazolyl)-thiophene; tpt or tPyTz, 2,4,6-tris(pyridin-4-yl)-1,3,5-triazine; TXyBim, 1,2,4,5-tetrakis(5,6-dimethylbenzimidazol-1-ylmethyl)benzene; xbp, 4,4′-(1,3-xylylene)-bis(3,5-dimethylpyrazole); XyBim, α,α′-bis(benzimidazol-1-yl)-*o*-xylene.

* Corresponding author. Tel.: +886 2 27898518; fax: +886 2 27831237.
E-mail addresses: kllu@gate.sinica.edu.tw, lu@chem.sinica.edu.tw (K.-L. Lu).

http://dx.doi.org/10.1016/j.ccr.2014.07.012

Keywords:
Cavity
Emission
Host–guest interactions
Metallacycles
Self-assembly

by engineering the different parts in neutral metal–organic ensembles, emissions from blue to red have been achieved. The neutral metallacyclic structures are unique in their well-defined forms and would be expected to function as a macrocycle host with a large internal cavity shapes generated by the tailored ligands. Hence, the presence of both photophysical properties and the cavity sizes of these neutral metallacycles make them intriguing hosts for neutral guests and metal ions. This *review* provides an overview of the structural features and properties of neutral discrete metal–organic cyclic architectures ranging from binuclear to fascinating multinuclear assemblies that emerged during the period from 2005 to 2012.

1. Introduction

The self-assembly of macrocyclic compounds has become an intensely active area of research in supramolecular chemistry because, not only of their internal cavities with well-defined shape and size, but also owing to their promising functionalities and applications [1–35]. To date, a large number of excellent examples of self-assembled macrocyclic molecules containing well-defined sizes and shapes have been reported, since the pioneering studies were reported [36–45]. The incorporation of transition metal centers into these macrocyclic host structures can confer new functionalities such as Lewis acidity, magnetism, redox activity or luminescence properties, thus providing potential applications of such materials as chemosensors, molecular recognition and electron transfer assemblies [46–67]. To construct more sophisticated molecular functions, systematically, chemically easy-to-modify building blocks have been identified. Maverick and co-workers [68,69] reported on the first self-assembled macrocyclic hosts derived from polydentate ligands with an aqueous solution of copper salts. The linkage of an organic moiety to these complexes controlled the size and shape of the inner cavity and permitted various guest molecules to be incorporated. Several general synthetic approaches to the preparation of discrete metallacycles have emerged, which include directional bonding [46,47], symmetry interactions [48,49], and weak-link approaches [50]. Many impressive examples of metallosupramolecular materials can be found in studies reported by Lehn [1,49,70], Sauvage [51], Stang [46,47], Fujita [26–31], Mirkin [50], Hupp [52–55], Lees [56–59], Lu [60,61], Jin [62,63], and others [64–67]. Lehn et al. demonstrated the spontaneous self-assembly of dinuclear helicates from bipyridine and copper (I) [70]. Elegant, pioneering studies by J.-M. Lehn, Fujita et al. in 1990 first demonstrated the utility of end-capped palladium(II) ions and 4,4′-bipyridine building blocks in the self-assembly of a molecular square in a quantitative yield and also resulted in the formation of 1:1 complexation with 1,3,5-trimethoxybenzene in water [71–73]. The Pt(II) and Pd(II) macromolecules were subsequently obtained in high yields by Stang's group by simply mixing the simple components [74,75]. The simplicity of self-assembly has resulted in a plethora of self-assembled complexes having structures containing higher-order cyclic species with nanometer-sized cavities [76–108]. Interestingly, most of the self-assembled compounds assembled from neutral nitrogen-based linkers and oxidized metal ions in the self-assembly process resulted in the formation of positively charged species. They exhibit good solubility in solvents and act as hosts for electron rich guests through electrostatic interactions and some solvent guests [46,47].

On the other hand, neutral assemblies could be designed in such a way, by selecting the appropriate neutral ligand and neutral precursor as a donor and acceptor, respectively, or by coordinating an anionic ligand with cationic or neutral metal centers. Their cavities do not contain free counter ions, which may complicate the assembled structures or may occupy part of the empty space [46]. Hence, neutral assemblies are expected to be more suitable hosts, especially for the encapsulation of neutral guests. To the best of our knowledge, the synthesis of neutral macrocycles in one-step reactions with cavities that are sufficiently wide to accommodate guest molecules are scarcely known, compared to charged assemblies. It is, therefore, timely and desirable to develop a new approach for producing neutral metallamacromolecules with well-defined shapes and sizes. Studies reported by Stang [46,47], Cotton [45,109–111], Mirkin [44,50], Severin [66,112–115], and Lu [60,61] focused on preparing various neutral functionalized assemblies, some of which showed catalytic activity and selectivity for different sized guest molecules.

The tuning of photophysical properties from the UV through the visible to the near IR could be achieved by varying the structure of the ligands used, as well as the metal ions present in the metal–organic architectures. These compounds offer interesting opportunities for incorporating different cavity sizes that can act as hosts for aromatic guests through π–π, hydrophobic interactions or producing a cavity with functional groups that can act as a hydrogen-bond donor or acceptor and would be expected to allow the selective uptake of hydrogen-bonding guests in addition to photochemical reactions and molecular devices. Although several reviews on the general topic of supramolecular chemistry have already appeared [46,47,60,116,117], the coverage of neutral metal–organic macrocycles is more limited. As the result of a review article, we concluded that much room exists for the placement of neutral metal–organic macromolecules and their properties. The aim of the present review is to provide an overview of the structural features and properties of neutral discrete metal–organic cyclic architectures ranging from binuclear to fascinating multinuclear assemblies in confined spaces that have emerged during the period from 2005 to 2012.

2. Design and synthetic strategies

The self-assembly approach driven by noncovalent interactions is the most popular and an efficient alternative method and offers considerable advantages over the classical synthetic route [75]. The critical conditions for the synthesis of metallacycles under thermodynamic control are: (i) the bonds must form only between active functional end group of the components, (ii) the bonds must be kinetically labile to allow for self-sorting and self-correcting processes, and (iii) the resulting species must be thermodynamically favored over competing species [118–120]. When building units are properly designed and preprogrammed, they spontaneously assemble into well-defined and kinetically labile, thermodynamically stable discrete supramolecular products in fewer steps. The kinetically labile coordinative bonds between the components provide for relatively defect-free, self-healing assemblies with a high structural integrity, as a result of the equilibrium between the components and final product [46,47]. Under proper synthetic conditions, the assemblage can undergo self-sorting and self-correcting processes until all of the components congregate