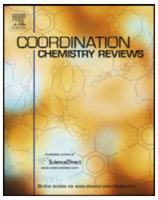
Coordination Chemistry Reviews 254 (2010) 2416–2428

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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



Review

Directed self-assembly of inorganic redox complexes with artificial peptide scaffolds

Carl P. Myers, Mary Elizabeth Williams*

Department of Chemistry, The Pennsylvania State University, 104 Chemistry Building, University Park, PA 16802, USA

Contents

---

* Corresponding author. Tel.: +1 814 865 8859; fax: +1 814 865 3292.
E-mail address: mbw@chem.psu.edu (M.E. Williams).

doi:10.1016/j.ccr.2010.02.018

ARTICLE INFO

Article history:
Received 2 November 2009
Accepted 15 February 2010
Available online 20 February 2010

Keywords:
Self-assembly
Oligopeptide
Peptide nucleic acid
Metal complexes
Photoinduced electron transfer
Aminoethylglycine
Redox
Electrochemistry

ABSTRACT

An ongoing challenge in the construction of supramolecular systems is controlling the relative geometry of functional redox species for molecular electronics devices, including wires, switches, and gates. This review focuses on the use of artificial peptide strands to assemble inorganic complexes that are redox active. These approaches toward macromolecular assembly use varying oligoamide backbones and assembly motifs that grew from earlier reports of single oligolysine or proline chains containing pendant redox species that undergo photoinduced charge separation. Recently, peptide nucleic acid chains that form double-stranded duplexes analogous to DNA by hydrogen bonding of complementary base pairs have been modified to contain metal complexes. In these structures, hydrogen bonding and metal coordination combine to form crosslinks between the PNA strands. Finally, a family of structures is described that is based on an aminoethylglycine scaffold with pendant metal coordination sites, but without intervening nucleic acid base pairs. These structures form multimetallic complexes that are either single- or double-stranded, or that form hairpin loop structures. These motifs for using artificial peptide strands for self-assembly hold electron donors and acceptors in relative positions that provide structural connectivity and permit electron transfers between linked metal complexes. This is a new approach for creating polyfunctional redox architectures that could ultimately enable the construction of potentially large and complex molecular electronics devices.

1. Introduction

Nature utilizes self-assembly to create macromolecules that are capable of performing the functions necessary for life. For example, photosynthetic organisms self-assemble supramolecular structures that are capable of undergoing electron transfer reactions after the absorption of a photon, leading to chemically functional charge separated states. In so doing, this multi-step process provides the necessary energy requirements to fuel biological systems. Making synthetic supramolecular analogs of biological electron transfer cascades may ultimately lead to molecular computing, photocatalysts, solar fuel production, etc. Much attention has been paid to this topic and several reviews describe approaches to this challenge that include organic [1–3] and inorganic [4–6] examples and others utilizing fullerenes and ruthenium compounds [7,8]. The synthetic challenge is to build large structures capable of long-range, sequential electron transfers that are robust and versatile. In this review, we describe tactics that, in combination, mimic two of the prevalent strategies in nature: self-assembly by molecular recognition, and the use of repeating units of amino acids to form larger peptides, proteins, and enzymes.

1.1. Synthetic mimics of biomolecules

Natural structures primarily rely on hydrogen bonding to assemble complex tertiary architectures. For example double-stranded (ds) DNA hybridizes by self-assembly using hydrogen bonding recognition of nucleic acid complements (e.g. A–T and G–C base pairing). The predominant approach in inorganic synthetic analogs is to rely on metal coordination chemistry as a means of self-assembly. For example, Hupp and coworkers self-assembled molecular squares and rectangles with Re carbonyl complex corners and symmetrical nitrogen heterocycles (e.g. 4,4′-bipyridine or pyrazine) walls [9]. This chemistry has been expanded to form assemblies with complex catalytic and photochemical properties [10–13]. Likewise, Stang and Cao have been instrumental in developing well-controlled assembly of molecular geometries using metal–ligand interactions, primarily with Pd and Pt [14]. These structures have been reported for potential applications in molecular recognition and catalysis [15–18].

Macromolecules that make up living organisms are built from repeating units. Nucleobases present in RNA and DNA along a sugar phosphate backbone with simple linkages can be arranged in any sequence and length. Like nucleic acids, proteins are comprised of amino acids; the sequence and type of modular repeating units define the function of the macromolecule. This review describes synthetic analogs that take inspiration from these, with the goal of using the versatility of modular units without the need for *de novo* synthesis of new structures. Together with metal coordination based self-assembly, polyfunctional and reconfigurable inorganic redox structures can be readily prepared.

1.2. DNA with “metallobase” pairs

Several research groups have replaced nucleic acid base pairs in duplex DNA with inorganic complexes, often called “metallobase” pairs, to produce hybrid assemblies. In this methodology, analogous to A–T and G–C Watson–Crick base pairs, ligands on opposite chains are “complementary” with respect to coordinative saturation of the metal center. For example, for a four-coordinate metal (e.g. Cu^{2+}, Zn^{2+}, or Pt^{2+}) the ligand pairs bidentate–bidentate (e.g. bipyridine–bipyridine, 2×2) or tridentate–monodentate (e.g. terpyridine–pyridine, 3×1) are complementary ligand pairs. Alternatively using octahedral metals such as Fe^{2+} or Co^{2+}, the tridentate–tridentate pair (e.g. terpyridine–terpyridine, 3×3) would be complementary.

Shionoya and coworkers designed a number of hybrid DNA systems that incorporate metal complexes into the sugar phosphate scaffold [19–23]. Meggers et al. incorporated artificial bases into DNA duplexes: in one example, dipic ligands were inserted in the oligonucleotide and Cu^{2+} formed coordinative crosslinks [24]. This structure was later crystallographically characterized as helical [25]. Additional refinements using this strategy incorporated Ag^{+} metal ions [26] and modified the backbone to glycol nucleic acid (GNA) [27]. A separate review in this issue by Shionoya describes metallobase pair modified DNA in detail.

1.3. Amino acid based structures

Amino acid building blocks provide a facile approach toward synthesizing large structures capable of performing redox processes. Polyamide backbones have the structural simplicity and programmability to synthesize a variety of structures that control the placement and identity of metal complexes and allow electronic communication between metal centers. When combined with chromophores, electron donors and acceptors, these structures can form the electron transfer cascades necessary for artificial photosynthesis. This review describes recent efforts that couple metal complexes with polyamides that ultimately will be used for the purposes of electron transfer in long-range cascades and forma-