

Note

Bridged multiclusters derived from the face-capped octahedral $[\text{Re}_6^{\text{III}}(\mu_3\text{-Se})_8]^{2+}$ cluster core

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Abstract

The face-capped octahedral cluster $\text{cis-}[\text{Re}_6(\mu_3\text{-Se})_8(\text{PEt}_3)_4(\text{MeCN})_2](\text{SbF}_6)_2$, site-differentiated with protecting PEt_3 and substitutionally labile MeCN ligands, reacts with bidentate ligands (L) 4,4'-bipyridyl, (*E*)-1,2-bis(4-pyridyl)ethene, and 1,2-bis(4-pyridyl)ethane to give the first examples of cluster-based molecular squares of the general formula $\text{cyclo-}[\text{Re}_6(\mu_3\text{-Se})_8(\text{PEt}_3)_4\text{L}]_4(\text{SbF}_6)_8$. The complexes were characterized by microanalysis, ^1H and ^{31}P NMR, and time-of-flight electrospray ionization mass spectrometry. Cyclic voltammetry reveals in each case one quasi-reversible oxidation and, for two compounds, one reversible and one irreversible reduction process. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The hexanuclear molybdenum and tungsten(II) halide complexes $[\text{M}_6\text{X}_8]^{4+}$ comprise a broad class of soluble transition element clusters, significant in themselves [1,2] and as precursors to multicluster supramolecular assemblies. The newly disclosed family of soluble $[\text{Re}_6^{\text{III}}\text{Q}_8]^{2+}$ (Q = S, Se, Te) clusters [3–5] sizeably extends their range. Explorations of $[\text{Re}_6\text{Se}_8\text{Br}_6]^{3-/-4-}$ and $[\text{Re}_6\text{Se}_8\text{I}_6]^{3-/-4-}$ substitution chemistry [6,7] have established controlled halide replacement protocols with non-labile triethylphosphine, generating site-differentiated species $[\text{Re}_6\text{Q}_8(\text{PEt}_3)_6-n\text{X}_n]^{(2-n)}$ ($n = 0-3$, Q = S, X = Br; Q = Se, X = I) not easily achieved with Group 6 analogue clusters. The rhenium–iodine bond is conveniently ruptured with silver(I) salts in coordinating media, producing, among other clusters, $\text{cis-}[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{MeCN})_2]^{2+}$ (**1**) [8]. We consider this cluster feasible for assembling un-

precedented cyclic multiclusters, and describe syntheses of ‘molecular squares’, which complement the growing gallery of nanoscopic supramolecules derivable from the ‘molecular library’ methodology [9] of Fujita [10], Stang et al. [11,12], and others [13–18].

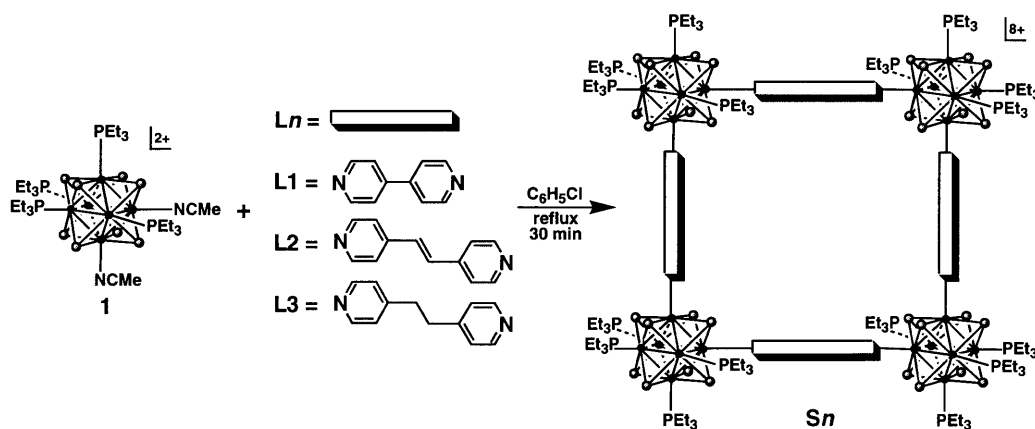
2. Experimental

2.1. General methods

Standard Schlenk and vacuum line techniques were employed for all manipulations of dioxygen- and/or moisture-sensitive compounds. Solvents were distilled from appropriate drying agents and degassed prior to use. Reagents were of commercial origin and were used as received. ^1H and ^{31}P NMR spectra of all compounds were determined with acetone- d_6 or acetonitrile- d_3 solutions with a Bruker AM-250 spectrometer, and were referenced to SiMe_4 (^1H) and 85% H_3PO_4 in H_2O (^{31}P). Low resolution ES mass spectra were obtained using an AX-505H mass spectrometer (JEOL USA, Inc., Peabody, MA). High resolution ES-MS were measured

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Scheme 1.

with a SX-102A mass spectrometer (JEOL USA, Inc., Peabody, MA) using a mass resolution of 10 000; the solvent was methylene chloride. Microanalytical services (carbon, hydrogen, and nitrogen) were provided by Desert Analytics Laboratory, Tucson, AZ.

2.2. Synthetic procedure

A mixture of *cis*-[Re₆Se₈(PEt₃)₄(MeCN)₂](SbF₆)₂ (**1**) (250 mg, 0.09 mmol) and **L_n** (0.09 mmol; 14.1, 16.4, and 16.6 mg for **L1** (4,4'-bipyridyl), **L2** ((*E*)-1,2-bis(4-pyridyl)ethene), and **L3** (1,2-bis(4-pyridyl)ethane), respectively) in 50 ml of dry chlorobenzene was refluxed under N₂ for about 30 min to produce orange–red crystalline solids and a pale-yellow supernatant. The solids were collected by filtration, washed with chlorobenzene (2 × 20 ml) and diethyl ether (5 × 10 ml), and dried under vacuum for 3 h. Products were obtained as reddish-brown crystalline solids: **S1** (243 mg, 94.7%), **S2** (235 mg, 90.7%), and **S3** (240 mg, 92.6%).

2.3. Cyclic voltammetry

Electrochemical measurements were performed in acetonitrile, with a PAR Model 263 potentiostat/galvanostat using a glassy carbon working electrode. The supporting electrolyte was 0.1 M [Bu₄N⁺][PF₆⁻]. Potentials were referenced to the standard calomel electrode. Redox potentials of compounds **S1**, **S2**, and **S3** were determined by cyclic voltammetry. Compounds **S1** and **S2** display reversible reductions near −0.8 V with irreversible reductions at more negative potentials. The −0.8 V reduction events of **S1** and **S2** exhibit anodic to cathodic peak separations (ΔE_p) of ~100 mV, which is comparable to that of ferrocene (136 mV), confirming that deviation from the theoretical value of 59 mV is owing primarily to uncompensated cell resistance. All three compounds undergo quasi-reversible oxidation at ca. 1 V. Values of the ratio of anodic and cathodic

current maxima I_a/I_c varied from 1.7 to 3.2. Anodic to cathodic peak separations (ΔE_p) for the oxidative processes are 200 mV (**S1**) and 167 mV (**S2** and **S3**).

3. Results and discussion

Scheme 1 illustrates the ‘molecular library’ approach applied to clusters. The procedure exploits the substitutional lability [19] of the acetonitrile ligands in **1**. Syntheses involve the stoichiometric reaction of **1** with a pyridyl-based bidentate ligand (**L_n**, $n = 1, 2, 3$) in refluxing chlorobenzene. Orange–red crystalline solids deposit after 30 min, leaving a pale-yellow supernatant due to the slight solubility of the product in chlorobenzene. With **L1**, **L2**, and **L3**, new compounds **S1**, **S2**, and **S3** were obtained, respectively. Analytically pure samples were isolated in high yields after washing (chlorobenzene followed by diethyl ether) and drying the solid products in air³. All three compounds are readily soluble in polar organic solvents, including dichloromethane, acetone, and acetonitrile, to yield or-

³ All ¹H NMR spectra were recorded in acetone-d₆. *Anal. Found:* C, 14.21; H, 2.54; N, 1.00. *Calc. for S1:* C, 14.33; H, 2.41; N, 0.98%. ¹H NMR: δ 1.07–1.24 (m, Me), 2.33 (q, CH₂), 2.43 (q, CH₂), 7.85 (d, β -H), 9.79 (d, α -H). ³¹P NMR: −23.1, −25.8. *ES-MS: m/z* 1152 ([Re₆Se₈(PEt₃)₂(L1)₂]²⁺), 1209 ([Re₆Se₈(PEt₃)₃(L1)₂]²⁺), 1268 ([Re₆Se₈(PEt₃)₃(L1)₂]²⁺), 1585 ([Re₁₂Se₁₆(PEt₃)₈(L1)₃]³⁺), 2613 ([Re₆Se₈(PEt₃)₄(L1)](SbF₆)⁺), 2691 ([Re₁₂Se₁₆(PEt₃)₈(L1)₃](SbF₆)₂⁺), 2769 ([Re₆Se₈(PEt₃)₄(L1)₂](SbF₆)₂⁺). *S2 Anal. Found:* C, 14.87; H, 2.69; N, 0.96. *Calc. for S2:* C, 15.02; H, 2.50%; N, 0.97%. ¹H NMR: δ 1.07–1.27 (m, Me), 2.32 (q, CH₂), 2.43 (q, CH₂), 7.65 (d, β -H), 7.72 (s, olefinic CH), 9.59 (d, α -H). ³¹P NMR: −23.6, −26.5. *ES-MS: see text. S3 Anal. Found:* C, 14.75; H, 2.46; N, 0.94. *Calc. for S3:* C, 15.03; H, 2.44; N, 0.97%. ¹H NMR: δ 1.10–1.26 (m, Me), 2.31 (q, CH₂), 2.42 (q, CH₂), 3.18 (s, CH₂), 7.43 (d, β -H), 9.48 (d, α -H). ³¹P NMR: −22.9, −26.2. *ES-MS: m/z* 1604 ([Re₁₂Se₁₆(PEt₃)₈(L3)₂]²⁺), 1682 ([Re₁₂Se₁₆(PEt₃)₈(L3)₂](SbF₆)²⁺), 1744 ([Re₁₂Se₁₆(PEt₃)₈(L3)₃](SbF₆)³⁺), 2640 ([Re₆Se₈(PEt₃)₄(L3)](SbF₆)²⁺), 2529 ([Re₆Se₈(PEt₃)₄(L3)₂](SbF₆)⁺).

ange–yellow solutions. New compounds were characterized by microanalysis, ^1H and ^{31}P NMR, and mass spectrometry; all three have resisted crystallization. In all cases, disappearance of the ^1H NMR signal at 2.69 ppm (acetone- d_6) of the coordinated acetonitrile ligands in **1** indicates quantitative substitution by the ditopic ligands. Appreciable downfield shifts were observed in the ^1H NMR of the bridging ligands upon coordination, owing to the inductive effect of rhenium(III). For example, the resonances of **L1** in **S1** shift by 1.0 (α -H, pyridyl, δ 9.8 ppm in **S1** vs. 8.8 ppm in **L1**) and 0.2 ppm (β -H, pyridyl, δ 7.9 ppm in **S1** vs. 7.7 ppm in **L1**) with respect to those of the free ligand (Fig. 1). Similar chemical shift changes occur for **L2** and **L3** upon binding (supplementary material). ^{31}P NMR spectra are consistent with symmetric assemblies (Fig. 1(b)). In each case, two ^{31}P peaks of equal intensity appear, indicating distinct sets of PEt_3 ligands, one in the plane of the square and the other perpendicular to it. No other ^{31}P signals were observed.

Time-of-flight electrospray mass spectra were collected to discern the degree of multicenter oligomerization. Electrospray ionization is the preferred technique for supramolecular compounds [9]; using ES-MS, we have previously characterized the quasi-linear tricluster $[\text{Re}_{18}\text{Se}_{24}(\text{PEt}_3)_{14}(\text{L1})_2](\text{SbF}_6)_6$, and related bridged diclusters [20]. Alternative methods involve more severe ionization processes or smaller available mass ranges. Fig. 2 depicts results for the representative compound **S2**. Of interest are peaks corresponding to multiclusters (assignments in parentheses) at m/z 1603.9 ($[\text{Re}_{12}\text{Se}_{16}$ -

$(\text{PEt}_3)_8(\text{L2})_2]^{3+}$), 1682.6 ($[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_8(\text{L2})_2](\text{SbF}_6)^{3+}$), 1743.9 ($[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_8(\text{L2})_3]^{3+}$), 1804.7 ($[\text{Re}_{18}\text{Se}_{24}(\text{PEt}_3)_{12}(\text{L2})_3]^{4+}$), 1863.2 ($[\text{Re}_{18}\text{Se}_{24}(\text{PEt}_3)_{12}(\text{L2})_3](\text{SbF}_6)^{4+}$), and 2640.9 ($[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_8(\text{L2})_2](\text{SbF}_6)_2^{2+}$). Fragment charges are deduced from m/z interpeak separations; for example, the signal at m/z 1603.9 is resolved as a sequence of smaller peaks ranging from ca. m/z 1595 to 1610, all spaced $1/3$ amu apart ($z = +3$). Peak structures associated with putative 4+ entities are more complicated, and may imply additional, more massive fragments coincident with those proposed. Parent ions were not observable for any of the three new compounds.

Mass spectral results for compounds **S1**–**S3** are equally consistent with bridged tetraclusters or with trimers. ^1H and ^{31}P NMR experiments indicate a single species prevalent in solution, which we believe to be tetrameric. In all known $[\text{Re}_6\text{Se}_8]^{2+}$ clusters, the angles between any two *cis*-oriented Re–(terminal ligand donor) bond vectors closely approach or equal 90° ; the N(1)–Re₆ centroid–N(2) angle in **1** is 88.1° [7]. This regularity should logically govern the present oligomers. A trimeric macrocycle would dispose bridging ligands at 60° to each other, straining the complex relative to the unstrained square. If trimers and tetramers equilibrate, entropy would favor the trimers (three tetramers \rightleftharpoons four trimers), and we do not at this juncture exclude their presence; they might coexist in solution with tetrameric **S1**–**S3** in such an equilibrium [14,21,22].

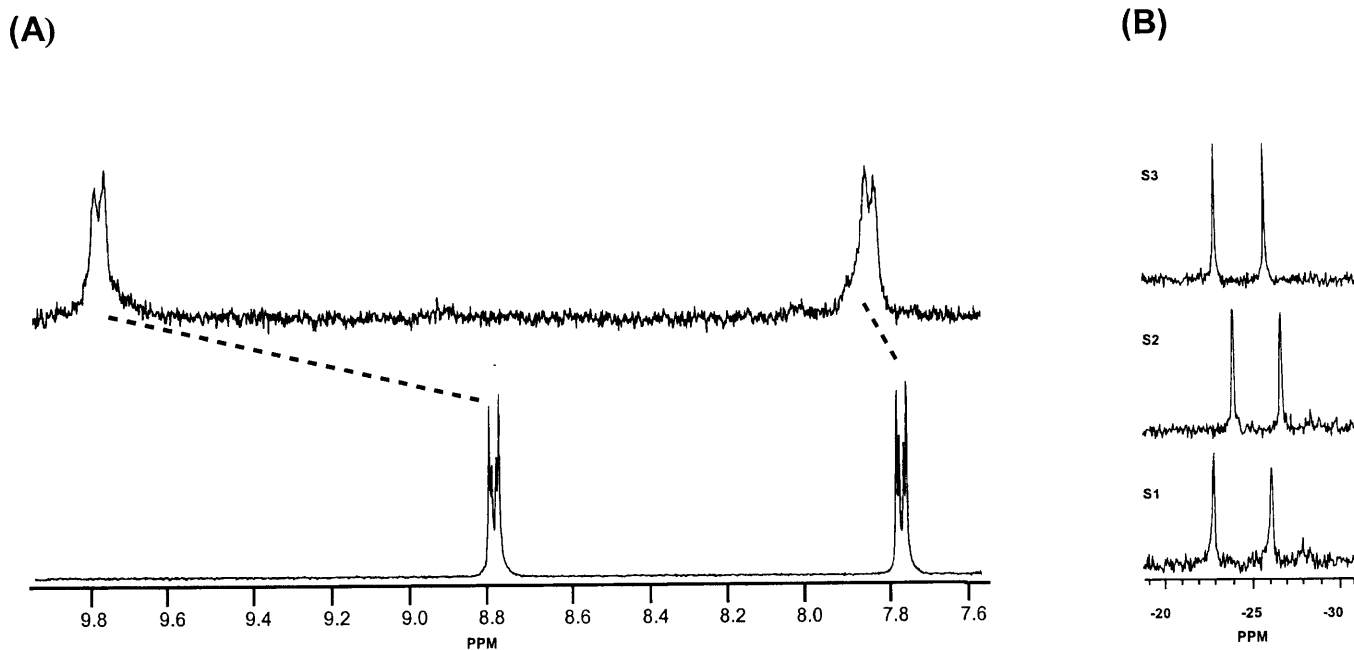


Fig. 1. (a) ^1H NMR spectra (acetone- d_6) of free **L1** (lower) and **L1** in **S1** (upper). Only the aromatic resonances are shown. See supplementary material for the full spectrum. (b) ^{31}P NMR spectra (CD_3CN , with 85% H_3PO_4 as reference) of **S1**, **S2**, and **S3**.

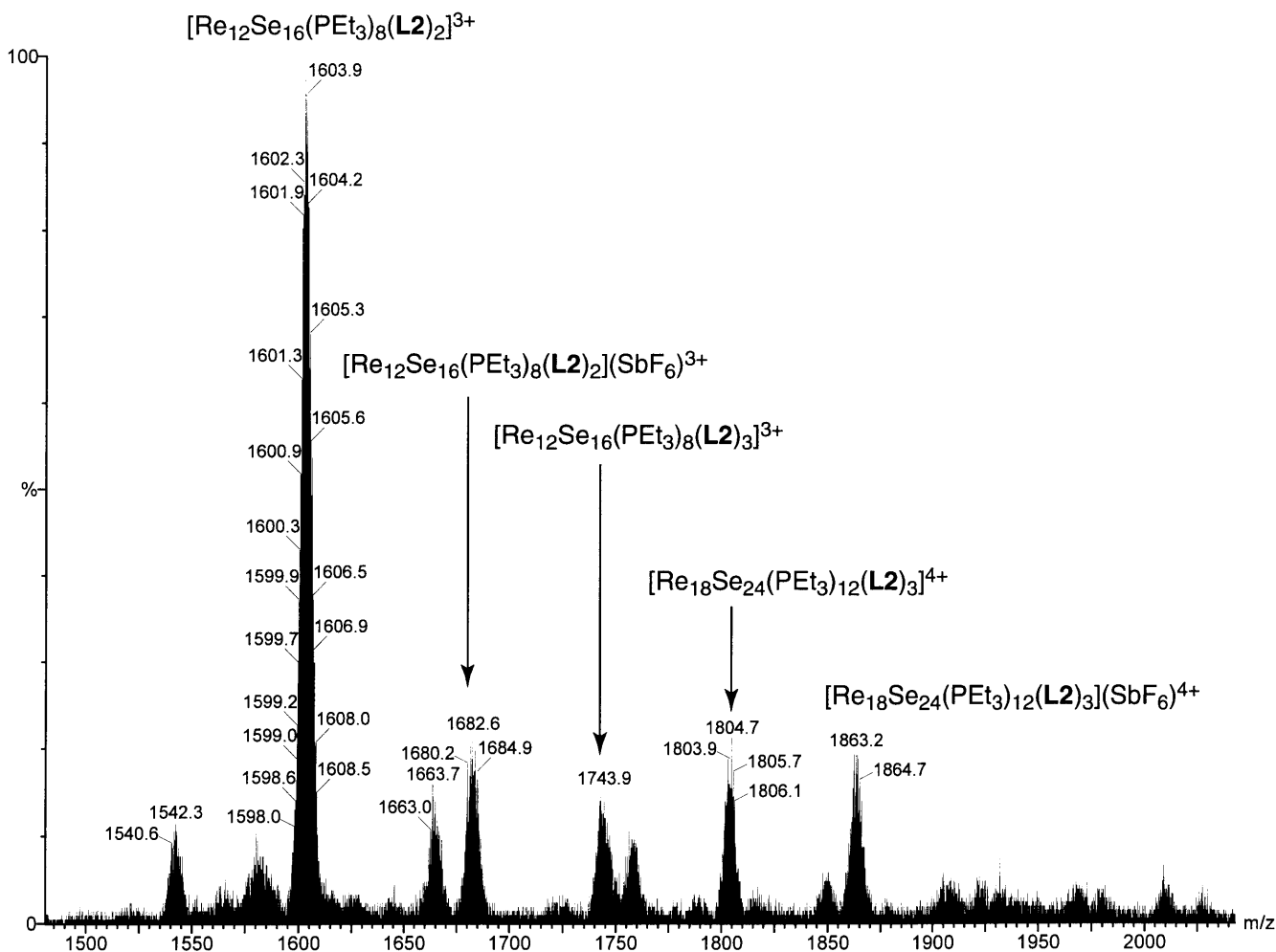
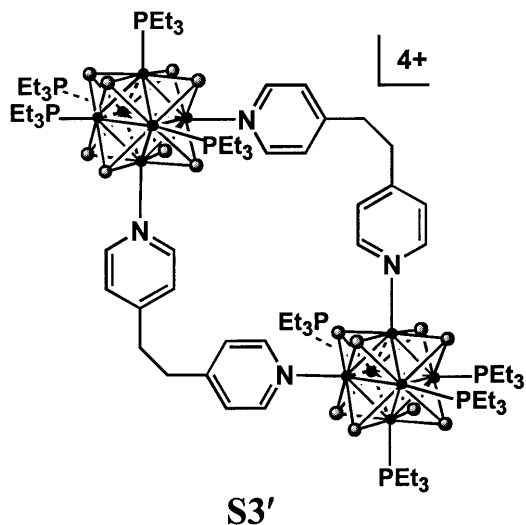


Fig. 2. Time-of-flight electrospray ionization mass spectrum of S2.

The flexible linker 1,2-bis(4-pyridyl)ethane in compound S3 poses special difficulties in characterization. While ostensibly much like S1 and S2, clear precedents [23,24] exist for a dimer of the kind S3':



Inspection of ES-MS results for S3 finds a signal corresponding to a triply charged cation at m/z 1743.8, assigned to $[\text{Re}_{12}\text{Se}_{16}(\text{PEt}_3)_8(\text{L}3)_3](\text{SbF}_6)^{3+}$. We cannot easily account for this fragment, with *three* ditopic ligands, in terms of the dimer S3'. Analogously to S1 and S2, we expect S3 to be predominantly tetrameric.

Cyclic voltammetry reveals a single process of chemically reversible oxidation ($E_{1/2} = 1.09$ V vs. SCE) in each case, from which no intercluster redox coupling is evident. This observation concurs with a similar result for bridged diclusters [20]. Clusters S1 and S2 also display reversible reductions near -0.8 V, with irreversible processes at more negative potentials. Observed redox events in S1–S3 are anodically shifted from those in anionic $[\text{Re}_6\text{Q}_8]$ clusters and neutral analogue compounds, a likely consequence of positive charge buildup. Reversible reductions (vs. SCE) at ca. -1.4 V in $[\text{Re}_6\text{S}_8\text{Cl}_4(\text{L}1)_2]^{2-}$ clusters [25], and at -1.2 and -1.4 V in neutral, non-cluster rhenium(I) carbonyl cyclophanes [26] were ascribed to electron uptake at bipyridyl ligands.

The molecular squares herein realize our earlier objective [6,20] of creating discrete, transition element-based supramolecules where polynuclear *clusters* surrogate for single metal ions (extended solid-state frameworks containing $[\text{Re}_6\text{Se}_8]^{2+}$ cluster building blocks have recently been reported [27]). The ‘molecular library’ approach [9] readily encompasses hybrid oligomers of clusters and mononuclear corners, and mixed-cluster squares as well. These spacious, highly charged tetramers suggest examination of potential host–guest chemistry [17]. Inviting prospects issue from $[\text{Re}_6\text{Se}_8]^{2+}$ phosphorescence [28,29], and these investigations are underway. The advent of $[\text{Re}_6\text{Se}_8]^{2+}$ -derived cyclophanes broadens the scope of such photophysical efforts markedly [30–32], and a confident outlook is warranted (after the completion of this work, there appeared an article describing syntheses and characterization of certain site-differentiated, phosphine-ligated W_6S_8 clusters [33]).

4. Supplementary material

Supplementary material is available from the authors on request.

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