

Built to Order: Molecular Tinkertoys from the $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ Clusters

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The creation of engineered molecular components for the assembly of electronic, photonic, and mechanical devices is the goal of nanotechnology.¹ Although the applications of such molecular machinery remain in the realm of speculation, great progress has been made in the development of various constructing elements. Most notable in this context is the large number of preprogrammed architectures produced with the use of transition metals in conjunction with polydentate ligands.² We envision an analogous yet probably more intriguing chemistry in which metal clusters are utilized in place of single metal ions.³ The significance of constructing cluster-supported supramolecules is two-fold: From a structural viewpoint, the availability of multiple metal sites in a cluster allows for stereochemically unique disposal of ligands in a supramolecular setting, a feature propitious to the creation of a variety of desired geometry. From the perspective of achieving certain useful functions, the inherent metal–metal or metal–ligand bonding interactions provide an opportunity for interesting and unique physical and chemical properties. Such efforts are thus expected to offer many fascinating research problems with potentially important ramifications.⁴

Of particular interest in this capacity are the $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ core-containing clusters,⁵ which have received considerable recent interest.^{6,7} With respect to mononuclear and other cluster-based starting materials, these face-capped octahedral clusters offer a number of structural and functional advantages when applied for the assembly of designed supramolecules. For example, unlike their well-known isomorphs of the earlier transition metal–halides/chalcogenides,⁸ the $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ clusters are stable to aerobic handling and vigorous synthetic conditions, yet labile enough that multiple-step, solution-phase syntheses are easily accomplished.^{6,7a} In addition, the stereochemistry about the Re(III) apexes can be selected and maintained throughout a particular chemical transformation.^{6,7a} Consequently, the desired geometry of a given assembly can be obtained with no possibility of rearrangement of the cluster building blocks.⁹ This stereochemical rigidity effectively eliminates the flexibility that frequently complicates the construction of supramolecules based on mononuclear² and dinuclear^{3a} complexes. From a materials perspective, the $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ clusters exhibit physical characteristics that may be useful in engineered substances. The cluster core is luminescent,^{7a,d,e} and the luminescence is dependent on the Re(III) coordination environment.^{7d} The redox potentials of various $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ clusters are also strongly affected by the nature of the ligands.^{5b,6c,7a} These interesting traits suggest that one might be able to tune the optical and electronic behavior of the final assembly. Equally tantalizing is the prospect of achieving novel properties due to the cooperative interactions between the cluster components.

Well-structured connecting pieces are also required to introduce branches, angles, or loops to the supramolecular cluster array of a

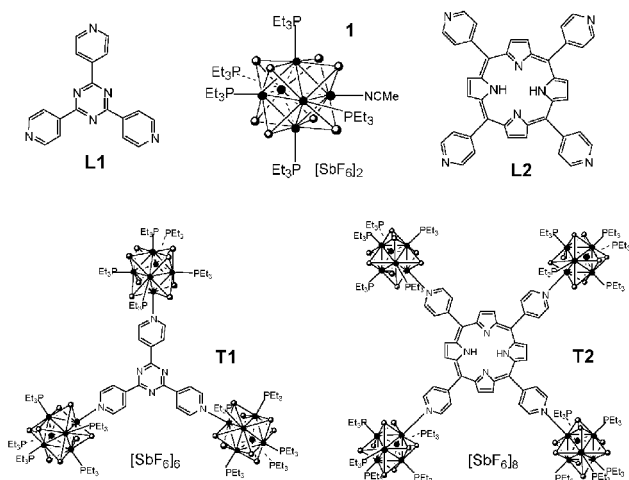


Figure 1. Molecular structures of the star-shaped multicusters (**T1** and **T2**) and their corresponding building blocks (**1**, **L1**, and **L2**).

desired geometry. Among the simplest connectors are the pyridyl-based linear or pseudolinear bidentate ligands. The ligands, 4,4'-dipyridyl, 1,2-bis(4-pyridyl)ethane, and (*E*)-1,2-bis(4-pyridyl)ethene have been used for the construction of dumbbell-shaped cluster dimers that feature two $[\text{Re}_6(\mu_3\text{-Se})_8(\text{PEt}_3)_5]^{2+}$ clusters capping the bridging ligands.^{6c} More recently, square-shaped tetraclusters have also been realized, wherein the aforementioned ligands serve as the edge of the molecular square.¹⁰ In this bridging capacity, star-shaped connectors carrying arms at fixed angles in a plane, such as **L1** and **L2** in Figure 1, may offer greater structural possibilities. Well-ordered two-dimensional structures may be generated by the attachment of clusters to the planar scaffold.¹¹ On the basis of this notion and by utilizing the $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ clusters and the star connectors as the construction kit's components, we have successfully created two molecular "Tinkertoys" whose synthesis and structural characterization are described in this report.

The synthesis of the multicuster stars (**T1** and **T2**, Figure 1) takes advantage of the substitutional lability of the Re-bonded nitrile molecule of $[\text{Re}_6(\mu_3\text{-Se})_8(\text{PEt}_3)_5(\text{CH}_3\text{CN})](\text{SbF}_6)_2$ (**1**)^{6a} with pyridyl-based ligands.^{6b,c,7c,10} Thus, reacting **1** with a stoichiometric amount of 2,4,6-tri-4-pyridyl-1,3,5-triazine (**L1**) and 5,10,15,20-tetra(4-pyridyl)-21H,23H-porphine (**L2**) in refluxing chlorobenzene produced the star-shaped tricluster (**T1**) and tetracluster (**T2**), respectively.

The molecular structure and stereochemistry of **T1** and **T2** are supported by several lines of spectroscopic evidence. Upon the formation of **T1**, for example, the ¹H NMR resonance of the coordinated nitrile of **1** disappears, indicating that the bonded solvent molecule is displaced. This is corroborated by the emergence of the α -H signal of the coordinated pyridyl moieties at 9.56 ppm (a, Figure 2), shifted from 8.94 ppm in free **L1**.

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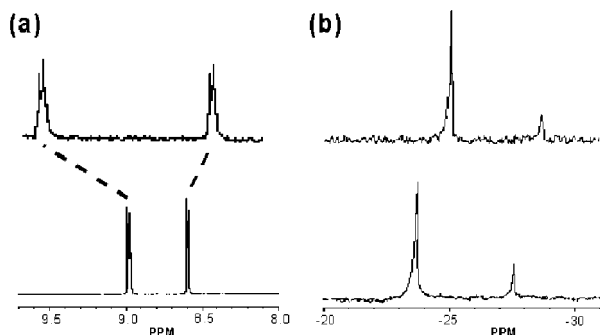


Figure 2. (a) ^1H NMR spectra of free **L1** (lower) and **L1** in **T1**. Only the aromatic resonances are shown. (b) ^{31}P NMR spectra of **1** (lower) and **T1**.

A noticeable but less dramatic chemical shift of the β -H atom of the pyridyl ring is also observed. The simplicity of the ^1H NMR spectrum is consistent with a highly symmetric structure of **T1**. Similar chemical shift changes occur for **L2** upon the formation of **T2** (Supporting Information). Lending further credence to the highly symmetric structure is the unsophisticated ^{31}P NMR spectrum of **T1** (b, Figure 2), which clearly show one type of terminal clusters with two ^{31}P resonance peaks (4:1 relative ratio) characteristic of a pentaphosphine substituted species. The identities of **T1** and **T2** are further confirmed by microanalysis (CHN) and electrospray ionization mass spectrometry. Interpretation of the mass spectra is straightforward as the corresponding molecular ion peaks are clearly identified.

Both **T1** and **T2** are readily soluble in dichloromethane, acetonitrile, and other common polar organic solvents to yield orange-red solutions. Single crystals of **T1** were obtained from a dichloromethane solution by vapor diffusion with diethyl ether. The mesmerizing structure of **T1**, shown in Figure 3, was established crystallographically.¹² The Re–Re, Re–P, Re–Se, and Re–N bond distances are unremarkably close to those reported for similar compounds.^{5–7}

Interesting properties may be anticipated for these multicenter arrays. For example, **T1**, possessing a three-fold rotational symmetry (*octupolar* chromophores), may display two-photon absorption properties¹³ as well as improved second-order nonlinear optical properties.¹⁴ Metal complexes of **T2** are expected to exhibit rich electrochemistry and catalytic properties, analogous to its polyru-

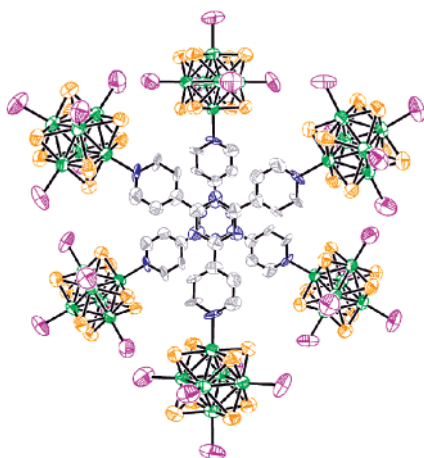


Figure 3. An ORTEP view (50% ellipsoids) showing two units of the cationic core of **T1** in a staggered disposition. Ethyl groups are omitted for clarity. Color legends: C(gray), N(blue), P(purple), Re (green), Se (brown). Inter-molecular stacking distance between the central aromatic rings is 11.27 Å.

thenated analogues.¹⁵ Electrochemical and photophysical studies of **T1**, **T2**, and various metal complexes of **T2** are underway.

In summary, we have presented the creation of two star-shaped $[\text{Re}_6(\mu_3\text{-Se})_8]^{2+}$ cluster assemblies emanating from a central planar connector. The synthetic approach, based upon stepwise buildup of metal clusters with organic fragments, offers the potential for exquisite control over the detailed architecture of the materials, which may lead to a variety of unusual shapes and novel properties.

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Supporting Information Available: Synthesis and characterization data for **T1** and **T2** (PDF). Tables of crystal data, structural solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **T1** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Merkle, R. C. *Nanotechnology* **2000**, *11*, 89.
- (2) See, for example: (a) Zaworotko, M. J. *J. Chem. Soc. Rev.* **1994**, *23*, 283. (b) Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (c) Fujita, M. *J. Chem. Soc. Rev.* **1998**, *27*, 417. (d) Caulder, D. N.; Raymond, K. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1185. (e) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1460. (f) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.
- (3) Supramolecular assemblies supported by metal–metal bonded dimeric units have recently been elaborated. See: (a) Cotton, F. A.; Lin, C.; Murrillo, C. A. *Acc. Chem. Res.* **2001**, *34*, 759. (b) Bera, J. K.; Smucker, B. W.; Walton, R. A.; Dunbar, K. R. *Chem. Commun.* **2001**, 2562. (c) Bonar-Law, R. P.; McGrath, T. D.; Singh, N.; Bickley, J. F.; Steiner, A. *Chem. Commun.* **1999**, 2457.
- (4) Alivisatos, A. P.; Barbara, P. F.; Castleman, A. W.; Chang, J.; Dixon, D. A.; Klein, M. L.; McLendon, G. L.; Miller, J. S.; Ratner, M. A.; Rossky, P. J.; Stupp, S. I.; Thompson, M. E. *Adv. Mater.* **1998**, *10*, 1297.
- (5) (a) Gabriel, J. C. P.; Boubekour, K.; Uriel, S.; Batail, P. *Chem. Rev.* **2001**, *101*, 2037. (b) Long, J. R.; McCarty, L. S.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 4603.
- (6) (a) Zheng, Z.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 2163. (b) Zheng, Z.; Holm, R. H. *Inorg. Chem.* **1997**, *36*, 5173. (c) Zheng, Z.; Gray, T. G.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 5173.
- (7) Selected references: (a) Chen, Z.-N.; Yoshimura, T.; Abe, M.; Sasaki, Y.; Ishizaka, S.; Kim, H.-B.; Kitamura, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 239. (b) Bennett, M. V.; Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 8022. (c) Wang, R.; Zheng, Z. *J. Am. Chem. Soc.* **1999**, *121*, 3549. (d) Gray, T. G.; Rudzinski, C. M.; Nocera, D. G.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 5932. (e) Arratia-Pérez, R.; Hernández-Acevedo, L. *J. Chem. Phys.* **1999**, *111*, 168. (f) Naumov, N. G.; Virovets, A. V.; Sokolov, N. S.; Artemkina, S. B.; Fedorov, V. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 1943.
- (8) Prokopuk, N.; Shriver, D. F. *Adv. Inorg. Chem.* **1999**, *46*, 1.
- (9) Site-differentiated, phosphine-ligated $\text{W}_6(\mu_3\text{-S})_8$ clusters have recently been reported. See: Jin, S.; Venkataraman, D.; DiSalvo, F. J. *Inorg. Chem.* **2000**, *39*, 2747.
- (10) Selby, H. D.; Zheng, Z.; Gray, T. G.; Holm, R. H. *Inorg. Chim. Acta* **2001**, *271*, 228.
- (11) *Modular Chemistry*, NATO ASI Series, Michl, J., Eds.; Kluwer: Dordrecht, The Netherlands, **1997**.
- (12) Structural analysis for **T1** at 170(2) K: Red rod, trigonal space group $P\bar{3}_1/c$, $a = 26.493(2)$ Å, $b = 26.493(2)$ Å, $c = 37.545(6)$ Å, $\beta = 120^\circ$, $V = 22822(4)$ Å³, $Z = 4$, $R1(wR2) = 0.0910(0.1962)$, $GOF = 1.115$.
- (13) Chung, S.; Kim, K.; Lin, T.; He, G. C.; Swiatkiewicz, J.; Prasad, P. N. *J. Phys. Chem. B* **1999**, *103*, 10741.
- (14) See, for example: (a) Zyss, J.; Ledoux, I. *Chem. Rev.* **1994**, *94*, 77. (b) Thalladi, V. R.; Brasselet, S.; Weiss, H.-C.; Bläser, D.; Katz, A. K.; Carrell, H. L.; Boese, R.; Zyss, J.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc.* **1998**, *120*, 2563.
- (15) (a) Anson, F. C.; Shi, C. N.; Steiger, B. *Acc. Chem. Res.* **1997**, *30*, 437. (b) Toma, H. E.; Araki, K. *Coord. Chem. Rev.* **2000**, *196*, 307.

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