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Communication

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Isomers of Metal–Organic Complex Arrays

Alejandro M. Fracaroli,[†] Kentaro Tashiro,*[,†] and Omar M. Yaghi*[,†,‡]

[†]International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

[‡]The Molecular Foundry, Materials Sciences Division, Lawrence Berkeley National Laboratory, and Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: Three metal–organic complex arrays (MOCAs) with a specific sequence of metal centers as well as that of amino acid units were synthesized. These MOCAs are also isomers exhibiting a gelation capability dependent on the location of the metal complexes in the arrays.

Selective synthesis of isomers very often requires sophisticated control of chemical reactions. One of the typical examples can be seen in the synthesis of multinuclear heterometallic complexes, where, because of the limitations of conventional synthetic methodologies, even a pair of isolated isomers composed of three kinds of metal centers has yet to be reported.[1,2] We have recently established a synthetic protocol for producing multinuclear heterometallic complexes, by which metal–organic complex arrays (MOCAs) containing a specific sequence of metal centers as well as of amino acids can be successfully done.[3] Here, we use this synthetic methodology to make a series of isomers of MOCAs based on heterometallic triads as the first reported set of isolated isomers with three kinds of metal centers. Consequently, we found that the sequence in these isomers plays the decisive role in determining their self-assembling behavior.

Considering the limited diversity among the metal complex monomers previously reported for MOCA synthesis as well as the low solubility of constructed arrays in various solvents so far, we designed a new and more soluble metal complex monomer based on a rhenium(I) phenanthroline complex linked with a L-glutamic acid side residue (Figure 1A).[4] To keep sufficient reactivity of the monomer at the coupling step on the resin, one L-alanine spacer unit was attached to the C terminal of the glutamic acid unit. ^1H NMR spectroscopy of a 1:1 mixture of the rhenium(I) monomer and another phenanthroline ligand in dimethyl-d_6 sulfoxide demonstrated the absence of ligand-exchange activity in the complex within 4 days (Figure S6 in the Supporting Information), an essential property of metal complex monomers needed to construct MOCAs. The rhenium(I) monomer was successively coupled in different order with ruthenium(II) and platinum(II) terpyridine complex monomers having a L-alanine–L-tyrosine dipeptide moiety (Figure 1B,C) to give three isomers of MOCA triads (Figure 1D–F).[4] When the Ru–Pt–Re triad (Figure 1D) is depicted as an illustrative example, matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry of the cleaved samples confirmed the stepwise formation of the Ru–Pt dyad (Figure 2B; m/z 2004.53 and 2005.67 for the expected and found values, respectively) followed by the Ru–Pt–Re triad (Figure 2C; m/z 2687.59 and 2687.52). Although the latter was contaminated with shorter arrays such as a benzoyl-capped Ru–Pt dyad (Figure 2C; H_2NCO–Ru–Pt–NHBz) because of the imperfect coupling of the deprotected Ru–Pt dyad on the resin with the rhenium monomer in solution, reverse-phase column chromatography of the cleaved mixture allowed us to isolate the triad in 21% overall yield with respect to the resin used (Figure 2D).[4] In a similar way, isomeric triads Ru–Re–Pt (Figure 1E) and Re–Ru–Pt (Figure 1F) were also obtained in 15 and 6%, respectively.[4]

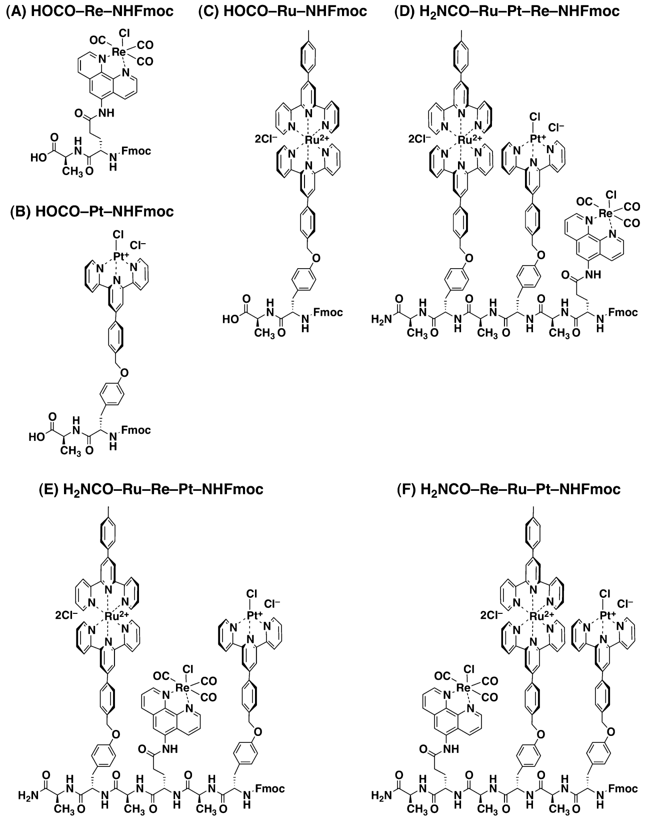

Figure 1. Molecular structures of (A–C) metal complex monomers and (D–F) isomers of MOCA triads.

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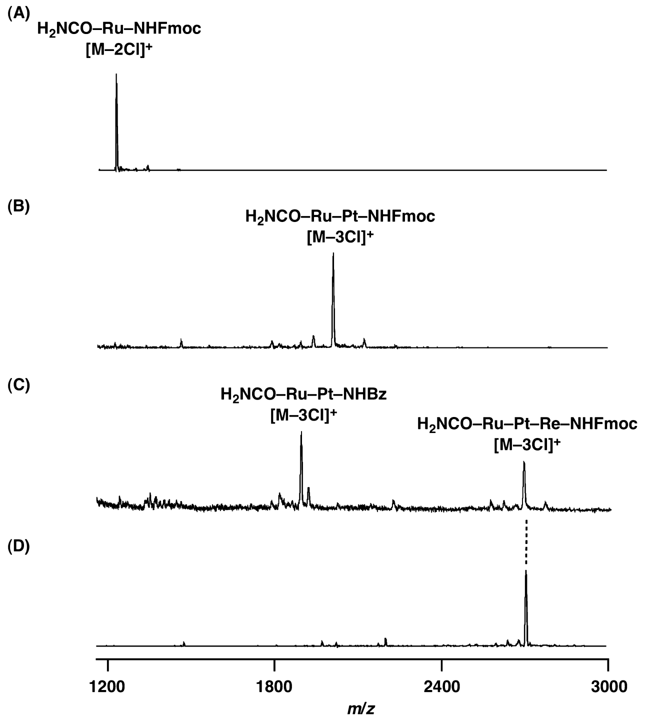

Figure 2. MALDI-TOF mass spectra as cleaved from the resin samples containing (A) a ruthenium monomer, (B) a Ru–Pt dyad, (C) a Ru–Pt–Re triad, and (D) the triad after reverse-phase column chromatography.

MALDI-TOF mass spectrometry of any of the three isolated triads showed fragmentation patterns similar to each other with a single dominant peak at m/z 2687–2688 (Figures 2D and S3 and S5 in the Supporting Information), reflecting that they are isomers composed of common building units. While ^{1}H NMR spectroscopy of the triads also displayed similarity among their spectral patterns, certain differences are observable in the shapes of the signals such as that appearing at δ 5.2–5.3, assignable to OCH_2 benzyl protons of the terpyridine moiety, because of the different order of the structural components (Figure S7 in the Supporting Information). The absorption spectra of the triads in MeOH at 20 °C also exhibited a detectable difference. When these spectra are normalized by the peak top absorbance of the metal-to-ligand charge-transfer (MLCT) band of ruthenium(II) terpyridine at 491 nm, the absorption band in the range of 380–430 nm, which includes the platinum(II) terpyiridine MLCT band, turns out to be the most and least intense for sequences Ru–Pt–Re and Ru–Re–Pt, respectively (Figure S8 in the Supporting Information). While the differences of the triads in their ^{1}H NMR and absorption spectra are only small, these isomers exhibit a contrasting self-assembling property. When a 1,2-dichloroethane/CF_3CO_2H/Et_3SiH solution (94:5:1, v/v/v) of the Re–Ru–Pt triad was evaporated to dryness and the residue was dissolved in MeOH, the resulting solution, initially homogeneous, formed a stable gel within 1 h of standing at room temperature (Figure 3C).[4,5] In sharp contrast, neither of the other two sequences displayed any sol–gel phase transition under identical conditions (Figure 3A,B). The phenanthroline-based organic moiety for the rhenium(I) complex monomer also exhibited a tendency to form gels, which suggests that the location of the rhenium(I) complex including the L-glutamic acid moiety in the arrays plays a crucial role in selectively giving the Re–Ru–Pt triad the observed gelation capability.

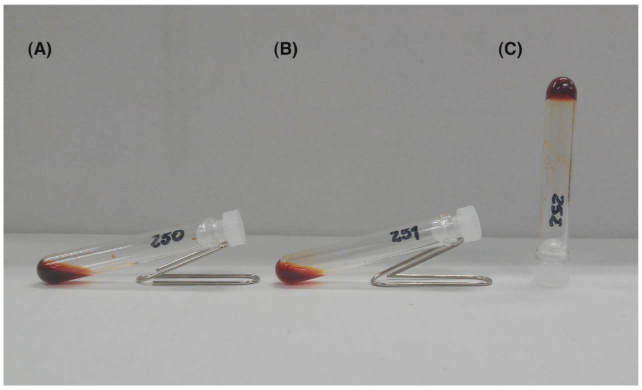

Figure 3. Photograph showing MeOH solutions prepared from (A) Ru–Pt–Re and (B) Ru–Re–Pt as well as (C) a gelified MeOH solution from Re–Ru–Pt. The concentrations of the triads in the samples are (A) 7.9, (B) 7.6, and (C) 7.9 mM.

In summary, by taking advantage of our methodology for the synthesis of heteronuclear multimetallic complexes, we constructed a series of isomers of the MOCA triad. These isomers serve as the first examples of isolated heteronuclear isomers with three or more kinds of metal centers. The sequence-selective gelation of the MOCA isomers, as observed in this study, is a good demonstration of how the sequence in a multimetallic complex can be finely controlled to impart a particular property on the complex.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, characterization, and gelation behavior of MOCA isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Tashiro.Kentaro@nims.go.jp (K.T.), oyaghi@lbl.gov (O.M.Y.). Fax: +81-29-860-4706. Tel: +81-29-851-3354-8429.

Notes

The authors declare no competing financial interest.

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