

Controlled Self-Assembly of Donor-Acceptor Molecules Directed by Metal-Metal Interactions

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1 Introduction

Construction of *p/n* molecular heterojunctions via self-assembly is a challenging issue, as it requires a sophisticated molecular design strategy to overcome attractive forces operative between donors and acceptors. Recently we found that the self-assembly of one enantiomer of a chiral donor-acceptor dyad successfully affords ambipolar nanofibers with large charge-carrier mobilities [1]. As a more universal approach, we proposed to make use of metal-metal interactions to control the self-assembly of donor-acceptor dyads, by expecting that the intrinsically homoselective nature of these interactions can induce segregation of donor and acceptor. As the first trial, we newly designed dyad **1** (Figure 1a) composed of cyclometalated organoplatinum(II) complex and fullerene, and its self-assembled structure was studied by means of X-ray crystallography [2].

2 Experiment

A covalently linked dyad of NCN pincer-type cyclometalated organoplatinum(II) complex and fullerene (**1**) was newly synthesized by NaOH mediated coupling of the corresponding organoplatinum(II) complex having a coordinated Cl anion with a fullerene bearing an alkyne unit, and unambiguously characterized by ¹H NMR, IR, and MALDI-TOF-MS analyses. **2** (Figure 1b) was prepared as reported.

Slow diffusion of hexane into a CS₂ solution of **1** or a toluene solution of **2** afforded red or yellow single crystals, respectively, suitable for X-ray crystallography. Single-crystal X-ray diffraction data were collected using Rigaku Mercury CCD system and processed with Molecular Structure Corporation model Crystal Clear software at beamline NW-2A of the Photon Factory-Advanced Ring (KEK, Japan). The diffraction images were processed by using HKL2000. Absorption correction was performed with the program PLATON. Each structure was solved by the direct methods using SHELXS-97 and refined by the full-matrix least-squares method on F₂ using SHELXL-97.

3 Results and Discussion

The ORTEP diagram of **1** proves that its organoplatinum(II) complex moiety has quite similar Pt(II)-C(sp), C(sp)-C(sp), and C(sp)-C(sp³) bond lengths with those of reference organoplatinum(II) complex **2** having no fullerene moiety [2, 3]. In accordance with these observations, the absorption spectrum of 1a or 1b in their good solvents such as CH₂Cl₂, is basically composed of the summation of the absorptions of the corresponding

two starting materials, showing the absence of detectable intramolecular ground state electronic interaction between organoplatinum(II) complex and fullerene moieties.

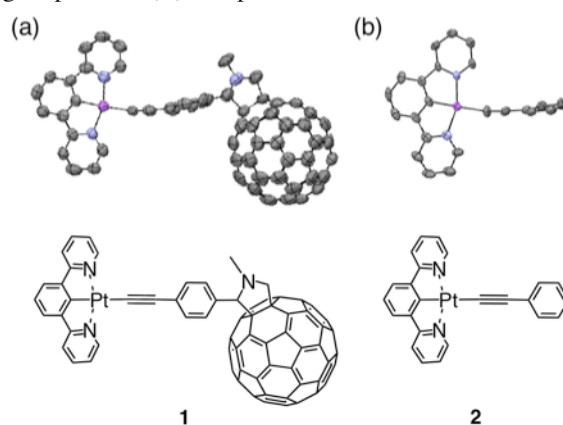


Fig. 1: Molecular structures and ORTEP diagrams of (a) **1** and (b) **2**. Hydrogen atoms are omitted for clarity.

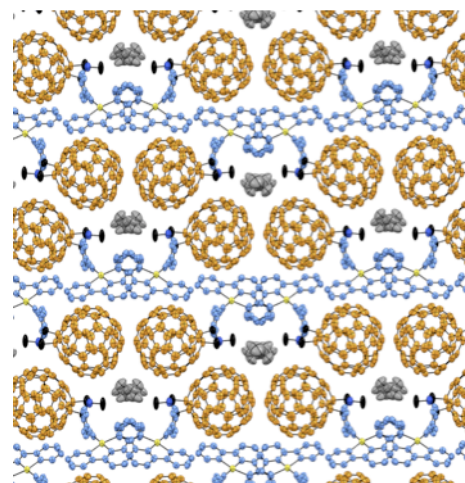


Fig. 2: ORTEP drawing (50% thermal ellipsoids) of the molecular packing of **1** in its single crystal. *C*-axis is located to be perpendicular to the presented cross section. Carbon atoms of its organoplatinum(II) complex and fullerene moieties are colored in blue and orange, respectively, while those of disordered hexane molecules are in grey. Hydrogen atoms are omitted for clarity.

X-ray crystallography on a single crystal of **1** revealed that the organoplatinum(II) complex and fullerene moieties of **1** are segregated to afford their alternating multilayers (Figure 2). Due to the presence of hexane molecules in the layers of fullerenes, however, their intralayer contacts are partly disturbed. Moreover, only one of the pyridyl rings of the pincer ligand exhibits a sign of the stacking interaction with neighboring organoplatinum(II)

complex moieties, suggesting that the packing structure of **1** would not be suitable for the evaluation of charge-transporting capability. In fact, no FET response was observed on the powder sample of crystalline **1**.

References

- [1] K. Tashiro *et al.*, *J. Am. Chem. Soc.*, 132, 6628–6629 (2010).
- [2] CCDC entry 1041759.
- [3] CCDC entry 1048124.

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