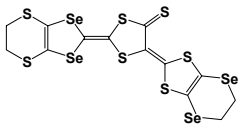
Template-free Growth of Nano/microcrystals of Magnetic Molecular Conductors by Electrochemical Oxidation of Bent Donor Molecules

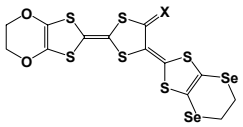
Xiangfeng Shao[1], Yuhta Yamaji[1], Toyonari Sugimoto[1], Hisashi Tanaka[2], Dominique de Caro[3], and Lydie Valade[3]
[1]*Department of Chemistry, Osaka Prefecture University, Japan*
[2] *Nanotechnology Research Institute, AIST, Japan*
[3]*Laboratoire de Chimie de Coordination du CNRS, France*
Email:toyonari@c.s.osakafu-u.ac.jp

Charge-transfer (CT) salts leading to molecular conductors and magnetic conductors are usually obtained as bulk crystals by electrochemical oxidation of donor molecules with a metal rod/plate anode in the presence of non-magnetic and magnetic supporting electrolytes. The use of several templates on the surface of anodes in the electrochemical oxidation occasionally gives nano/microcrystals of CT salts.[1]

We now found preferential formation of nano/microcrystals of CT salts of new bent donor molecules, ethylenedithiodiselenadithiafulvalenothioquinone- and ethylenedioxytetrathia-fulvaleno-thioquinone(-quinone)-ethyelenediseleno-1,3-dithiolemethides (**1**, **2** and **3**), which have tendency to form highly one-dimensional stacking structures, by using a platinum rod electrode with a diameter of 1 mm. When **1** was electrochemically oxidized in PhCl–EtOH containing NBu_4•$FeCl_4$ at 30 ºC, $\mathbf{1}_2$•$FeCl_4$ was obtained as nanowires with 300–400 nm in thickness and width, and several millimeters in length. While, the electrochemical oxidation of **2** in PhCl–EtOH and of **3** in 1,2-dichloroethane (DCE) containing NBu_4•$FeCl_4$ at –5 ºC gave $\mathbf{2}_2$•$FeCl_4$ and $\mathbf{3}_2$•$FeCl_4$•$(DCE)_{0.5}$,[2] both of which are microplates with 2–3 μm in thickness and 80–150 μm in width. The electrical conducting and magnetic properties of these nano/microcrystals are reported.



1



2: X = S
3: X = O

[1] J.–P. Savy, D. de Caro, L. Valade, T. Sugimoto *et al.*, New J. Chem. 31 (2007) 519.
[2] X. Shao, Y. Yamaji, H. Fujiwara, T. Sugimoto, J. Mater. Chem., in press.