Results in Physics 5 (2015) 74–75

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.journals.elsevier.com/results-in-physics

Microarticle

Formation of a green-form TTF–CA charge transfer complex confirmed with terahertz transmission spectrum

Takenori Tanno [a,*], Takahiro Oohashi [b]

[a] Venture Incubation Center, Akita University, 1-1 Tegatagakuen-machi, Akita 010-8502, Japan
[b] Graduate School of Environmental Studies, Tohoku University, 6-6-20 aza-Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan

ARTICLE INFO

Article history:
Received 18 February 2015
Accepted 6 March 2015
Available online 12 March 2015

Keywords:
Terahertz spectroscopy
Charge transfer complex
TTF–CA
Solid-state reaction

ABSTRACT

The green polymorph of tetrathiafulvalene–*p*-chloranil (TTF–CA) charge transfer complex was synthesized by grinding fine powders of TTF and CA. The polymorph was identified using terahertz spectroscopy.

Introduction

Equimolar mixture of tetrathiafulvalene (TTF) and *p*-chloranil (CA) form a charge transfer complex (CTC) by cosublimation or slow cooling of the solution [1]. The resulting green form (or green phase) of TTF–CA refers to the typical mixed stack TTF–CA complex. The black polymorph of TTF–CA has also been reported in the literature [1].

In our previous research [2], terahertz spectroscopy was used to determine the polymorph form of the complex, with co-grinding of TTF and CA resulting in the black form of the TTF–CA complex. The solvent-free process provides the means for high-yield CTC production. Following this result, several articles [3–5] have reported that solvent-free co-grinding of TTF and CA gives the green-phase of TTF–CA, not the black form, which is obtained only when the components are ground with a small amount of solvent. These reports provide further confirmation of the solid-state reaction product of TTF and CA.

Experimental

In this study, the synthesis was carried out in a globe box, purged with dry air. TTF and CA were purchased from TCI (Tokyo, Japan). Terahertz transmission spectra were obtained using a TSS-I terahertz spectrometer (Terahertz Laboratory, Inc., Akita, Japan). Other experimental details are the same as those described in our previous report [2].

Results and discussion

Fig. 1 shows the color of the TTF, CA, and their product, the TTF–CA complex. The TTF–CA complex was green. Fig. 2 presents the terahertz transmission spectrum for the TTF–CA complex; significant absorption peaks were observed at 1.4 and 2.3 THz. These features are characteristic of the green form of the TTF–CA complex [2]. From these results and previous reports [2–5], we concluded that the solid-state reaction of TTF and CA gives the green-form of the TTF–CA complex.

The discrepancy between the results in our previous report [2] and the results presented here remains unclear. Contamination and humidity may have contributed to the inconsistency. TCI, our TTF and CA manufacturer, verified that they have not implemented any changes in their production process since the time of our previous study. Finally, we wish to emphasize the usefulness of terahertz spectroscopy for observing the reaction and identifying the solid-state reaction product.

* Corresponding author. Tel./fax: +81 (0)18 889 2803.
E-mail address: tanno@gipc.akita-u.ac.jp (T. Tanno).

http://dx.doi.org/10.1016/j.rinp.2015.03.003
2211-3797/

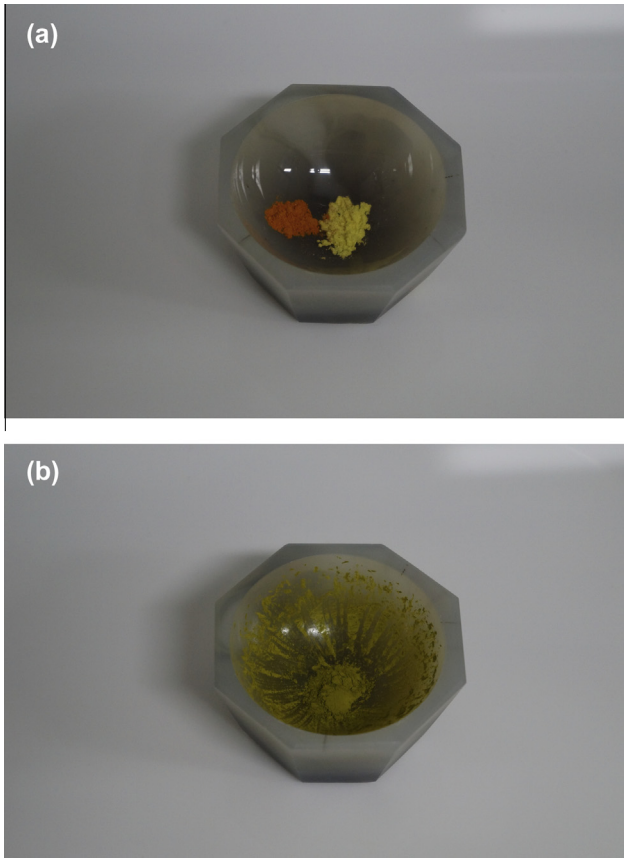

Fig. 1. Photographs of (a) TTF (right, yellow) and CA (left, orange); and (b) the TTF + CA mixture after being ground for 20 min. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

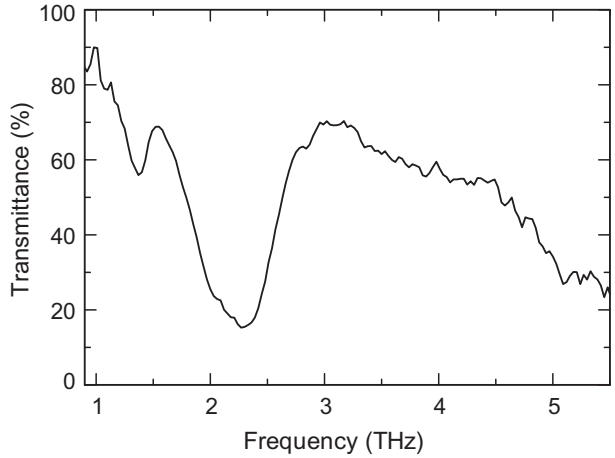

Fig. 2. Terahertz transmission spectra of the TTF + CA mixture after being ground for 20 min.

Acknowledgements

The authors thank Ms. Kyoko Umeno (Akita University) for her technical support. This work was conducted as part of a research project "Institute of Terahertz Waves Technology" (Akita University) and was supported by KAKENHI-26870063.

References

[1] Girlando A, Marzola F, Pecile C, Torrance JB. Vibrational spectroscopy of mixed stack organic semiconductors: neutral and ionic phases of tetrathiafulvalene–chloranil (TTF–CA) charge transfer complex. J Chem Phys 1983;79:1075–85.
[2] Nishizawa J, Tanno T, Oohashi T, Watanabe H, Oyama Y. Observation of the solid-state formation of a TTF–CA complex by terahertz spectroscopy. Synth Met 2008;158:278–82.
[3] Benjamin S, Pagola S, Huba Z, Carpenter E, Abdel-Fattah T. Solvent-drop assisted mechanochemical synthesis of the black and green polymorphs of the tetrathiafulvalene-chloranil charge transfer salt. Synth Met 2011;161:996–1000.
[4] Lapidus SH, Naik A, Wixtrom A, Massa NE, Ta Phuoc V, Del Campo L, et al. The black polymorph of TTF–CA: TTF polymorphism and solvent effects in mechanochemical and vapor digestion syntheses, FT-IR, crystal packing, and electronic structure. Cryst Growth Des 2014;14:91–100.
[5] Wixtrom A, Buhler J, Abdel-Fattah Tarek. Mechanochemical synthesis of two polymorphs of the tetrathiafulvalene-chloranil charge transfer salt: an experiment for organic chemistry. J Chem Educ 2014;91:1232–5.