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Supporting Information

Ultra-broad near infrared photoluminescence from (K-crypt)$_2$Bi$_2$ single crystal containing $[Bi_2]^{2-}$

Hong-Tao Sun,*[a] Tetsu Yonezawa,[a] Miriam M. Gillett-Kunnath,[b] Yoshio Sakka,[c] Naoto Shirahata,[c,d] Sa Chu Rong Gui, [e] Minoru Fujii,[e] and Slavi C. Sevov*[b]

[a] Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan. Fax: +81-11-706-7881; E-mail: timothyhsun@gmail.com

[b] Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, USA. Fax: +1 (574) 631-6652; E-mail: ssevov@nd.edu

[c] Advanced Ceramics Group, Advanced Materials Processing Unit, National Institute for Materials Science (NIMS), 1-2-1 Sengen, Tsukuba-city, Ibaraki 305-0047, Japan

[d] PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan

[e] Department of Electrical and Electronic Engineering, Kobe University, Kobe 657-8501, Japan

Synthesis of $[K\text{-}(2,2,2\text{-crypt})]_2[Bi_2]$

General Experimentals:

All manipulations were carried out under nitrogen using standard Schlenk-line and glovebox techniques. Ethylenediamine (Alfa-Aesar, 99 %) was distilled over sodium metal and stored in a gastight Schlenk under nitrogen in the glovebox. Toluene was dried over copper-based catalyst and 4 Å molecular sieve columns (Innovative Technology) and then stored over molecular sieves in the glovebox. 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Acros, 98%), was used as received after carefully drying under vacuum. Precursors with nominal compositions K_5Bi_4 were synthesized by heating the corresponding mixture of the elements (K: +99 %, Strem; Bi: 99.999 %, Strem) at 500 ^oC for 24 hr in sealed niobium containers that were jacketed in evacuated fused-silica ampoules.[1]

Synthesis of [K-(2,2,2-crypt)]$_2$[Bi$_2$] This compound was previously reported,[2] however, high clean yields were irreproducible. A solution of 2 – 2.5 ml of distilled ethylenediamine and 0.3 mmol (99 mg) 2,2,2-crypt were pipetted into 0.1 mmol (103 mg) of the K_5Bi_4 precursor in a 13 x 100 test-tube fitted with a stir bar. The solution was then stirred for 15 minutes at room temperature resulting in a bright green-blue solution. The reaction mixture was centrifuged for 5 minutes and filtered *via* a glass fiber pipette. Previously,[2] about 3 – 4 ml of additional toluene was slowly layered unto the bright blue-green solution in each test-tube and set aside for crystallization by slow diffusion. However, very little co-crystallized products of $[Bi_2]^{2-}$,[2] $[Bi_4]^{4-}$,[3] and lots of black precipitate resulted leading to difficulty in isolating large quantities of the

targeted $[Bi_2]^{2-}$ crystals for further analysis. Thus, to eliminate the further oxidized product of $[Bi_4]^{4-}$ and cleaner crystallizations, the following were carried out: (1) freshly distilled ethylenediamine was used every time; (2) the reaction was stirred for a maximum of 15 minutes and immediately centrifuged for 5 minutes; (3) the filtrate was evenly separated into three 40 cm (O.D. = 1 cm) crystallizing tubes and carefully layered with three parts toluene followed by two parts hexane. The tubes were then tightly capped and set aside for crystallization by slow diffusion. After several days, large dark red-brown plates (sometimes cubes or blocks) cleanly crystallized out without any residual black precipitate. The different morphologies were indexed and confirmed to be the same unit cell as those of the previously reported $[Bi_2]^{2-}$.[2] The crystallizing tube was then fitted with a nitrogen gas inlet and attached to a Schlenk-line, where all volatiles were evacuated off. The intact, dried, dark red-brown plates were then sealed under vacuum.

References:

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2. Gascoin, F.; Sevov, S. C. *J. Amer. Chem. Soc.* **2000**, *122*, 10251
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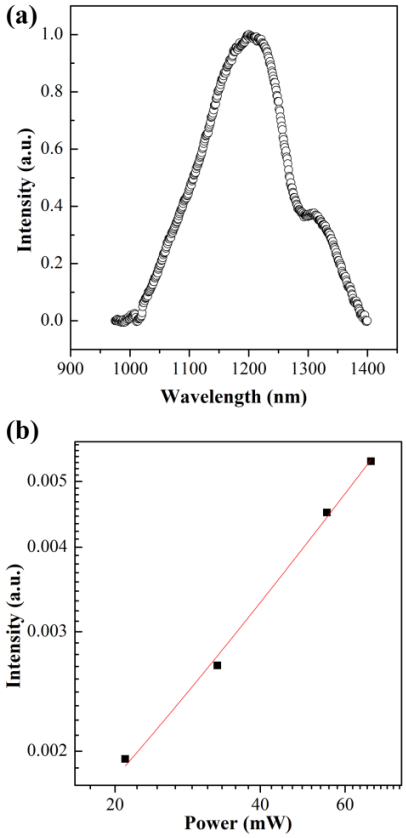

Figure S1. (a)The PL spectrum of $(K\text{-crypt})_2Bi_2$ crystals with excitation by the 514.5nm line of an Ar^+ laser. (b) Log–log dependence of the emission intensity at the peak wavelength on the excitation power of the 514.5 nm light. The slope is unity.