(a) **Experimental details**

**Boron nitride nanotubes:** The synthesis of multiwalled BN nanotubes has been accomplished via a carbon-free CVD reaction between Mg-B$_2$O$_2$ precursor and ammonia. [C. Tang, Y. Bando, T. Sato and K. Kurashima, Chem. Commun. 2002, 1290.] The structures, defects and sample purities were evaluated in the published communication. The oxidation at 700 °C and reduction at 1000 °C of the BN nanotubes were carried out in a horizon furnace in oxygen and hydrogen flows for 2 hours, respectively.

**Boron-nitrogen-oxygen complex:** The basic boric acid-diethanolamine complex 1 was prepared through a condensation reaction. Boric acid (0.1 mol) was mixed with diethanolamine (0.1 mol) and heated at 70 °C until a transparent viscous liquid formed. A solid condensation product was then dehydrated in an evaporator with a low pressure (50 mmHg) and a high temperature (165 °C) over 24 hours. Elemental analysis (%) calcd for 1: B 8.26, C 36.69, H 7.70, N 10.70; Found: B 8.25, C 36.86, H 7.81, N 10.79. FTIR vibrations of ~1400 (C-O), ~1070 (B-O), ~3400 (OH), ~710 and ~530 cm$^{-1}$ (O-B-O) were considered.

**Complex coordinated with NH$_2$- and N$^3$:** a mixture of 1 (2 g) and ethylenediamine or trioctylamine (30 mL) was loaded into a 50-mL teflon-lined stainless steel autoclave in a nitrogen atmosphere, heated to 180 °C and kept for 24 hours, to obtain yellow liquids. Compared with 1, FTIR gave the new vibrations in ~1370 and 770 cm$^{-1}$ (B-N), ~720 and ~600 cm$^{-1}$ (N-B-O$_2$) for both coordinated liquids, and ~1600 and ~2400 cm$^{-1}$ (N-H) for the ethylenediamine product, with a nearly disappeared OH vibration.

**Boron-nitride-oxide polymer:** Polymer contained BO$_2^-$ species was prepared by further condensation of 1 in trioctylamine up to 327 °C in a stainless steel autoclave. After the reaction for 4 days, the product was washed by trioctylamine for several times in a N$_2$ glove box, forming an air-sensitive solid that appears red to the eyes.

**Boron nitride crystals doped with BO:** Hexagonal BN crystals with BO$^-$ doping were prepared by reacting the polymer with ammonia at 900 °C for 2 hours and with oxygen
at 700 °C for 5 hours to remove carbon. The crystallization of BN was finally improved by annealing at 1500 °C for 5 hours in an argon flow. The treatment process might reduce the oxygen content by evaporating BO_x vapor, like,

\[ \text{BO}_2^- \rightarrow \text{BO}^- + \text{BO}_x \ (\nu) \]  

The detail about the transfer from BO_2^- to BO^- keeps unclear in this moment.

The oxidation effect for BN nanotubes was examined by transmission electron microscopy (TEM, JEOL 3010F). Cathodoluminescence spectrum was measured in the system that consists of a scanning electron microscope, a single monochromator, and a liquid-helium-cooled charge-coupled device. The content of C, N, H was analyzed by conventional elemental analysis and B by ICP. FTIR was measured by an infrared spectrometer (MAGNA-IR). The room-temperature photoluminescence spectrum and diffuse reflection spectrum were measured by a fluorescence spectrophotometer (Hitachi; F-5700) and an UV-VIS spectrophotometer with an integrating sphere (JASCO; Ubest V-560), respectively.

(b) **Oxidation of boron nitride nanotubes**

(a) High-resolution TEM picture showing a disorderly distribution of boron oxygen particles generated by oxidizing pure BN nanotubes in a flowing oxygen and (b) the corresponding EDS analyses.