**Significance:** Anthraquinodimethane-type extended tetrathiafulvalenes (TTFAQs) are known for having a rigid, non-planar, saddle-like structure in the neutral state. Here the authors demonstrate the ability of this class of extended tetrathiafulvalenes to act as selective metal cation sensors, in particular Ba2+.

**Comment:** Uncomplexed 1 shows a quenched fluorescence due to electron transfer between the electron-donating, thiafulvalene-containing unit, and the electron-accepting anthracenes. The reduced electron-donating capabilities experienced upon crown ether–cation binding, suppresses the electron transfer, ‘turning on’ fluorescence.