

The endohedral Ce<sup>III</sup>/Ce<sup>IV</sup> redox couple in the nitride clusterfullerenes

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Lanthanide-based nitride clusterfullerenes M<sub>3</sub>N@C<sub>2n</sub> with the same carbon cage isomer are usually barely distinguishable in their redox behaviour, which can be well understood taking into account the cage-based oxidation and reduction processes.<sup>1,2</sup> All exceptions from this behaviour, such as reduction of Sc<sub>3</sub>N@C<sub>80</sub> itself<sup>3-5</sup> or both reduction and oxidation of TiM<sub>2</sub>N@C<sub>80</sub> (M = Sc, Y),<sup>6-8</sup> are explained by the redox activity of the endohedral cluster.<sup>9</sup>

Recently we have reported that CeLu<sub>2</sub>N@C<sub>80-I<sub>h</sub></sub> is a notable exclusion from this principle.<sup>10</sup> Whereas its reduction behavior is similar to that of other nitride clusterfullerenes with the C<sub>80-I<sub>h</sub></sub> carbon cage, the oxidation potential of CeLu<sub>2</sub>N@C<sub>80</sub> is shifted cathodically by 0.6 V with respect to the oxidation potentials of other M<sub>3</sub>N@C<sub>80-I<sub>h</sub></sub> clusterfullerenes. This peculiar redox behavior was explained by the unprecedented redox activity of endohedral cerium (III), which was reversibly oxidized into the Ce(IV) state. In this work, we report on the recent progress in the further exploration of the redox behavior of Ce in nitride clusterfullerenes.

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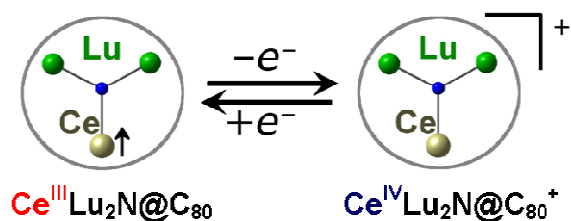


Fig. 1 Schematic description of the endohedral Ce(III)/Ce(IV) redox couple