## Photoswitchable azopyridine macrocyclic structure on bioacitve glass for controlled release of Ca<sup>2+</sup>

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Mesoporous bioactive glass nanoparticles (BGnPs) are a versatile tool not only for the development of new therapeutics also they provide a highly versatile support for the development of materials with site-selective functionalities<sup>1</sup>. The drawbacks of the BGnPs are the uncontrolled release of the ion on the medium which could limit their practical applications<sup>2</sup>. The photoisomerization of azobenzene has attracted attention in different fields to enable the photocontrolled activation of molecules. Some studies have modified mesoporous silica nanoparticles to create "gate keepers" trying to overcome the premature leakage of drugs and ions, and also to manipulate their release in a controllable manner<sup>3</sup>. Herein, we report a macrocyclic structure containing azopyridine group immobilized on the out-layer surface BGnPs for the release and capture of  $Ca^{2+}$ . The macrocycle structure consists of an azopyridine chelating unit, and a siloxy group for immobilization on the BGnP.

The modified BGnPs (EL1) were dissolved in artificial saliva and the solution was treated with alternating UV and LED irradiation every 15 and 30 min. The concentration of  $Ca^{2+}$  was analyzed by a  $Ca^{2+}$  sensor obtaining a "zig-zag" behavior after being irradiated every 30 min. It was observed that  $Ca^{2+}$  concentration increased once the light radiation switched from UV to LED. Isomeric forms (*trans* and *cis*-were found to display different affinities for  $Ca^{2+}$ , hence realizing an efficient on/off method for the release of calcium under light irradiation.

Furthermore, the EL1 conserve their potential of hydroxyapatite layer formation and buffer capacity. Unlike precedent methods, the present system could be applicable to a variety medical area such as dentistry.

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