

## **Supporting Information**

# **Boronate Ester Hydrogels for Biomedical Applications: Challenges and Opportunities**

*Léa Terriac,<sup>1</sup> Jean-Jacques Helesbeux,<sup>2</sup> Yves Maugars,<sup>1</sup> Jérôme Guicheux,<sup>1</sup>  
Mark W. Tibbitt,<sup>3</sup> Vianney Delplace\*<sup>1</sup>*

<sup>1</sup>Nantes Université, Oniris, CHU Nantes, INSERM, Regenerative Medicine and  
Skeleton, RMeS, UMR 1229, F-44000 Nantes, France

<sup>2</sup>Univ Angers, SONAS, SFR QUASAV, F-49000 Angers, France

<sup>3</sup>Macromolecular Engineering Laboratory, Department of Mechanical and Process  
Engineering, ETH Zurich, 8092 Zurich, Switzerland

**Table S1- Potential PBAs and diols for innovative BE hydrogel design.**

	PBA	Primary amine containing molecule	Diol	Product	Reversibility	Ref.
					none	1
Iminoborionate ester formation					Low reversibility $K_{eq, \text{ iminoboro.}} = 1100 \text{ M}^{-1}$ $K_{eq, \text{ BE}} = 2.45 \times 10^3 \text{ M}^{-1}$	2
					Not measured but mentioned and implied through glucose sensitivity	3
		–			$K_{eq}=166 \text{ M}^{-1}$	4
Boronate esters using salicylic acid derivatives		–			Low reversibility $K_{eq}=1.6 \times 10^4 \text{ M}^{-1}$	5

## References

- (1) Palvai, S.; Bhangu, J.; Akgun, B.; Moody, C. T.; Hall, D. G.; Brudno, Y. In Vivo Targeting Using Arylboronate/Nopoldiol Click Conjugation. *Bioconjugate Chemistry* **2020**, *31* (10), 2288–2292. <https://doi.org/10.1021/acs.bioconjchem.0c00453>.
- (2) Chapin, B. M.; Metola, P.; Lynch, V. M.; Stanton, J. F.; James, T. D.; Anslyn, E. V. Structural and Thermodynamic Analysis of a Three-Component Assembly Forming *Ortho*-Iminophenylboronate Esters. *The Journal of Organic Chemistry* **2016**, *81* (18), 8319–8330. <https://doi.org/10.1021/acs.joc.6b01495>.
- (3) Hu, J.; Hu, Q.; He, X.; Liu, C.; Kong, Y.; Cheng, Y.; Zhang, Y. Stimuli-Responsive Hydrogels with Antibacterial Activity Assembled from Guanosine, Aminoglycoside, and a Bifunctional Anchor. *Advanced Healthcare Materials* **2020**, *9* (2), 1901329. <https://doi.org/10.1002/adhm.201901329>.
- (4) Miki, R.; Yamaki, T.; Uchida, M.; Natsume, H. Diol Responsive Viscosity Increase in a Cetyltrimethylammonium Bromide/Sodium Salicylate/3-Fluorophenylboronic Acid Micelle System. *RSC Advances* **2022**, *12* (11), 6668–6675. <https://doi.org/10.1039/D1RA08831A>.
- (5) Martínez-Aguirre, M. A.; Flores-Alamo, M.; Yatsimirsky, A. K. Thermodynamic and Structural Study of Complexation of Phenylboronic Acid with Salicylhydroxamic Acid and Related Ligands. *Applied Organometallic Chemistry* **2018**, *32* (8). <https://doi.org/10.1002/aoc.4405>.