

## Supporting Information

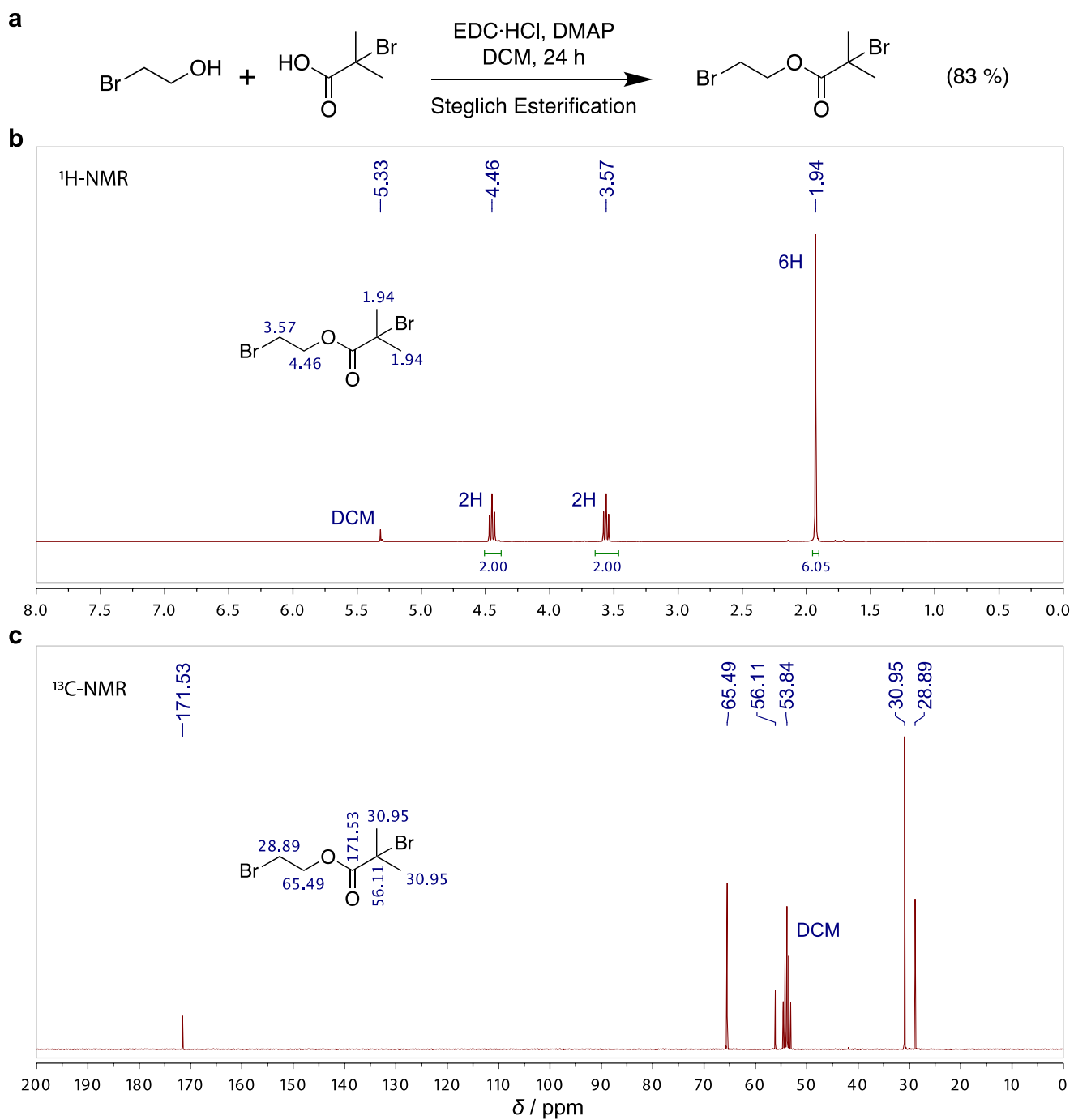
### **Versatile Surface Modification of Hydrogels by Surface-Initiated, Cu<sup>0</sup>-Mediated Controlled Radical Polymerization**

Kaihuan Zhang,<sup>†</sup> Wenqing Yan,<sup>†</sup> Rok Simic,<sup>†</sup> Edmondo M. Benetti,<sup>†,‡</sup> and Nicholas D. Spencer<sup>\*,†</sup>

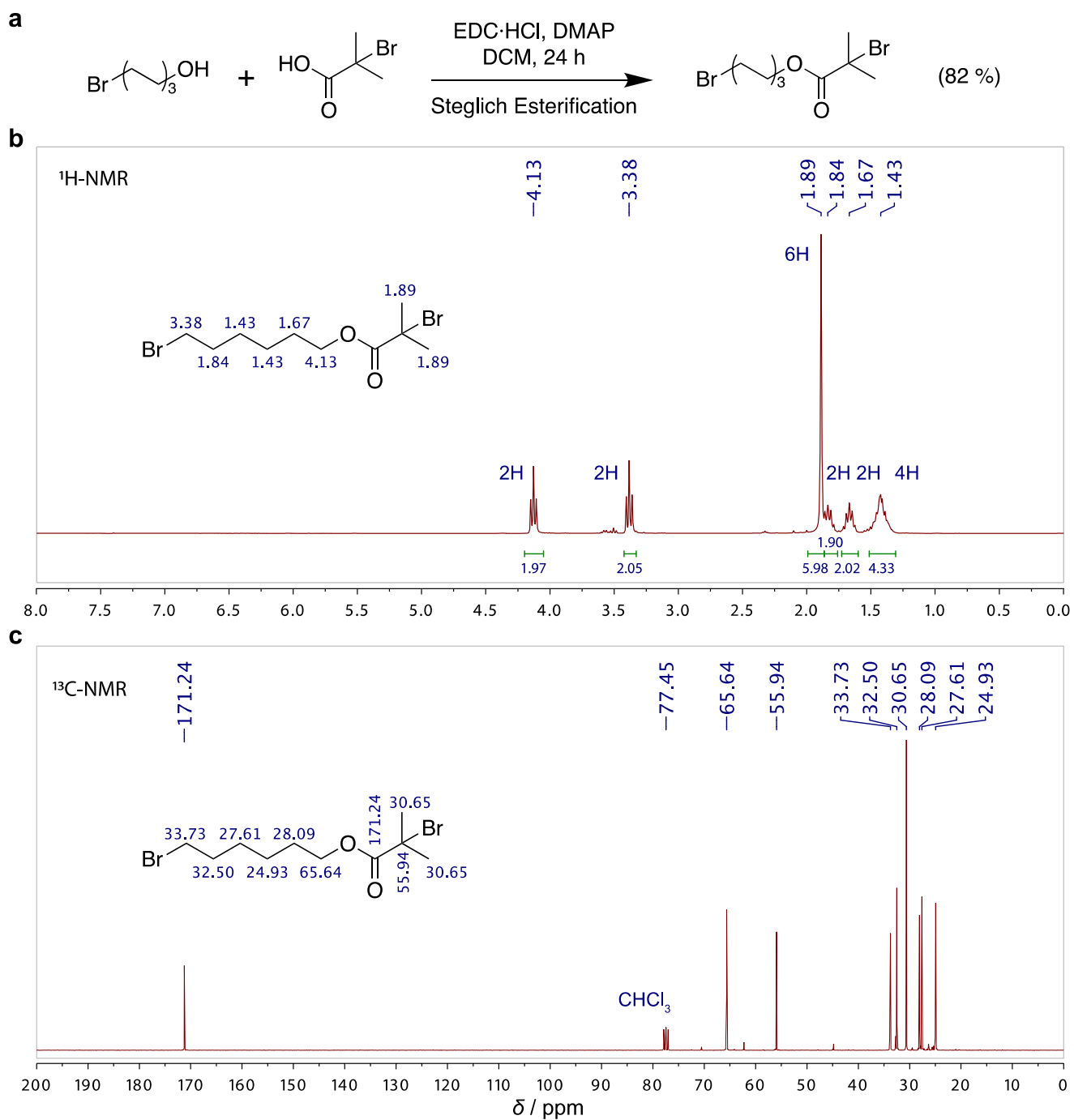
<sup>†</sup>Laboratory for Surface Science and Technology, Department of Materials, ETH Zurich, 8093 Zurich, Switzerland.

<sup>‡</sup>Biointerfaces, Swiss Federal Laboratories for Materials Science and Technology (Empa), 9014 St. Gallen, Switzerland.

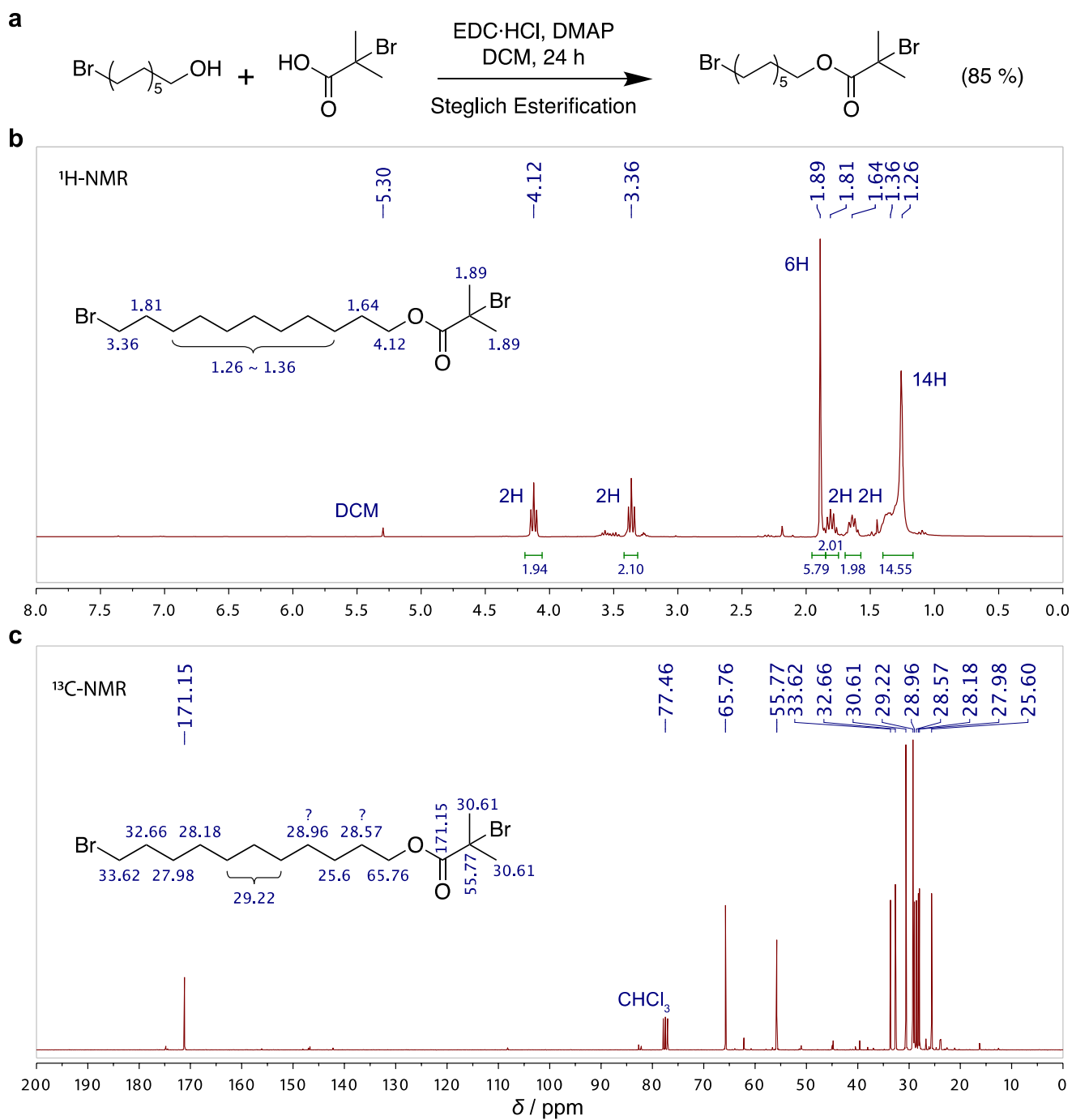
\*E-mail: [nspencer@ethz.ch](mailto:nspencer@ethz.ch)



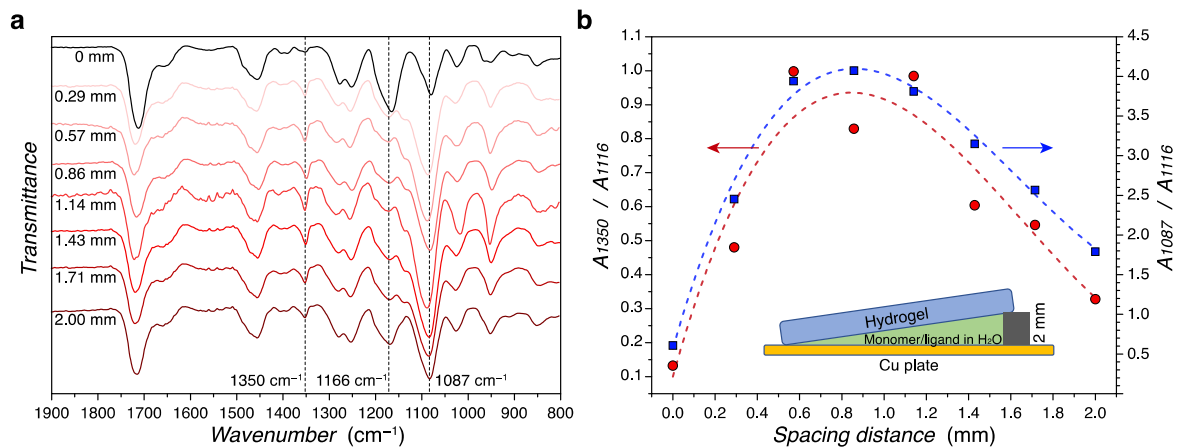
**Figure S1.** (a) Synthesis route, (b)  $^1\text{H}$  NMR and (c)  $^{13}\text{C}$  NMR spectra of C2-Br modifier.



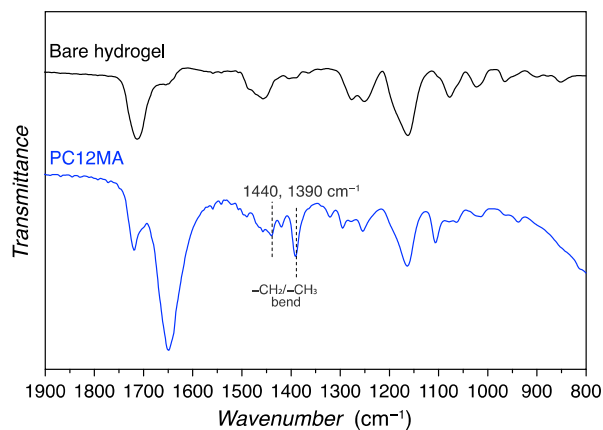
**Figure S2.** (a) Synthesis route, (b) <sup>1</sup>H NMR and (c) <sup>13</sup>C NMR spectra of C6-Br modifier.



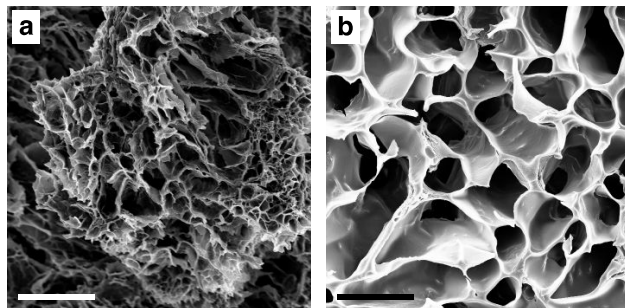
**Figure S3.** (a) Synthesis route, (b) <sup>1</sup>H NMR and (c) <sup>13</sup>C NMR spectra of C11-Br modifier.



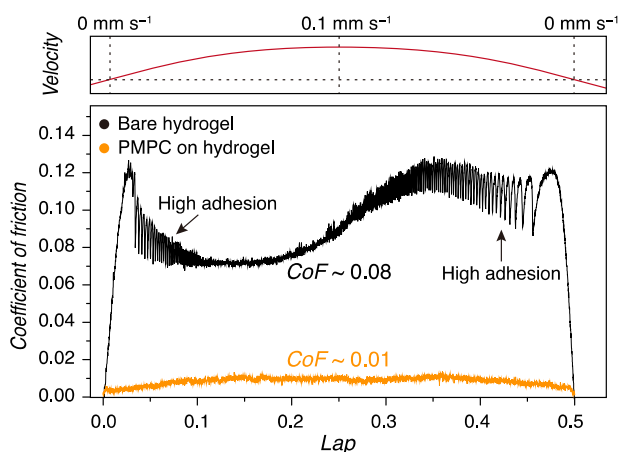
**Figure S4.** (a) ATR-FTIR spectra of POEGA polymer brushes prepared by using a tilted copper plate with spacing distance between 0 mm and 2 mm. Absorbance at  $1087\text{ cm}^{-1}$  and  $1350\text{ cm}^{-1}$  are attributed to the C–O stretching and C–H bending for POEGA, respectively. (b) Variations of the absorbance at  $1350\text{ cm}^{-1}$  (red) and  $1087\text{ cm}^{-1}$  (blue) for POEGA as a function of the spacing distance. The absorbance at  $1116\text{ cm}^{-1}$  was used as a reference for the purpose of normalization.



**Figure S5.** ATR-FTIR spectra of bare hydrogel and PC12MA polymer brush-modified hydrogel.



**Figure S6.** SEM images of (a) p(HEMA-NVP-DMAEMA) hydrogel and (b) PMETAC-modified hydrogel surface (scale bars: 10  $\mu\text{m}$ ). The bulk structure of p(HEMA-NVP-DMAEMA) hydrogel exhibited a homogeneous and compact structure with smaller pore sizes, while the surface of PMETAC-modified hydrogel showed a large porous structure due to the high water content.



**Figure S7.** Representative friction loop obtained by a reciprocating pin-on-disc friction test for the bare hydrogel and PMPC polymer brush-modified hydrogel (load 0.6 N, track distance 10 mm, sliding velocity 0.1  $\text{mm s}^{-1}$ ). The tests were performed at room temperature with hydrogel samples fully immersed in milli-Q water.