Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information for

The potential scarcity, or not, of polymeric overall water splitting photocatalysts

Benedict Saunders, Liam Wilbraham, Andrew W. Prentice, Reiner Sebastian Sprick, Martijn A. Zwijnenburg

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.

Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, U.K.

Email: m.zwijnenburg@ucl.ac.uk

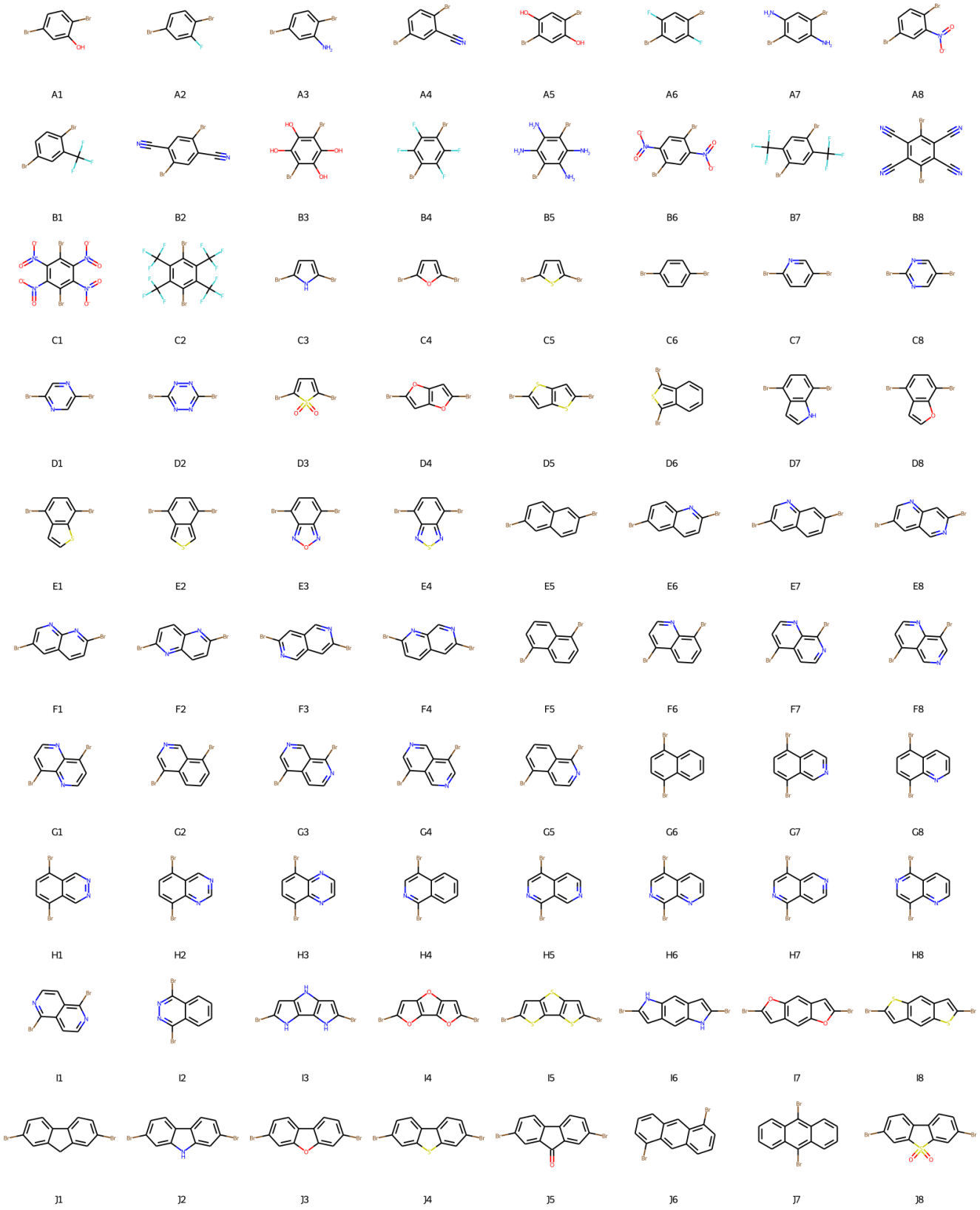

Fig. S1 *Overview of all monomers considered.*

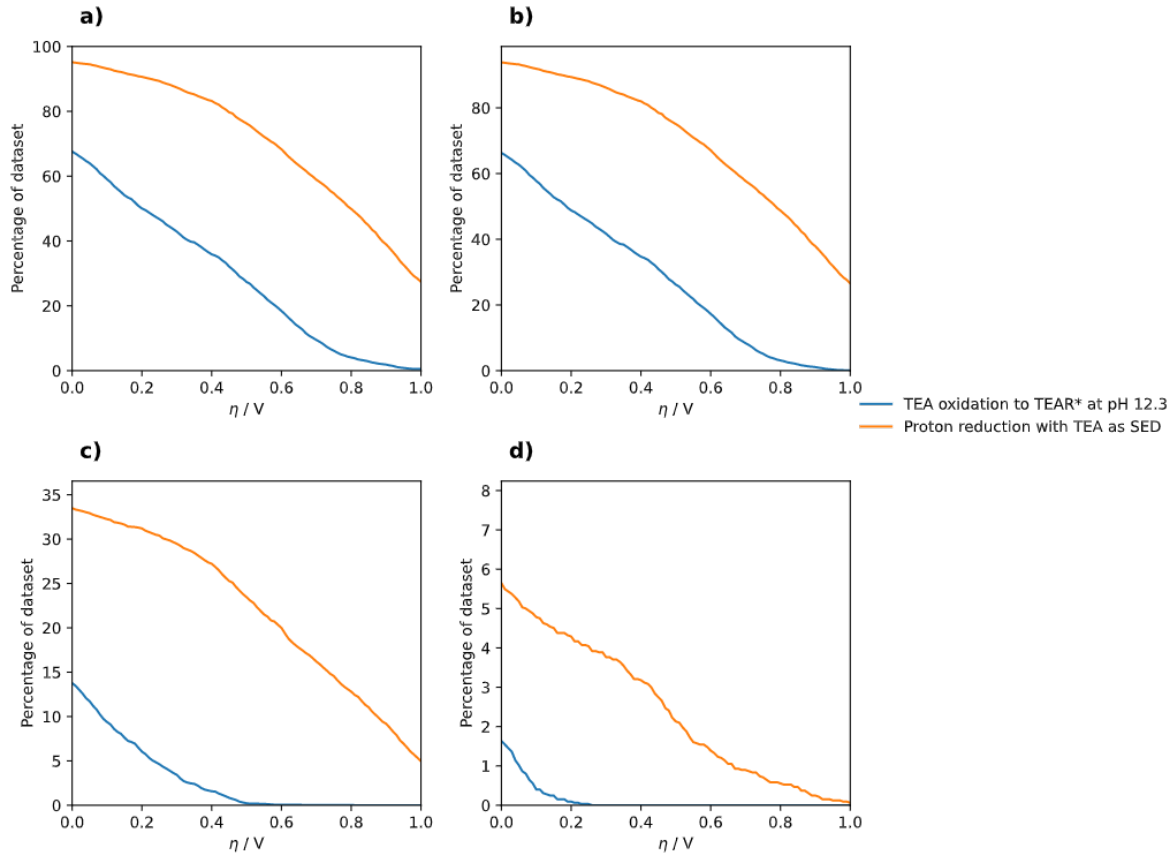

Fig. S2 *Percentage of (co-)polymers in the dataset that are predicted to be able to drive the reduction of protons and the overall oxidation of TEA (orange line) and the one-hole oxidation of TEA (blue line) at pH 12.3 for different optical gap ranges. Panel a) does not include a limitation on the optical gap. Panel b) introduces a limitation such that the predicted optical gap must be ≤ 3.5 eV, which is reduced to 2.5 eV in plot c) and finally 2.0 eV in plot d).*

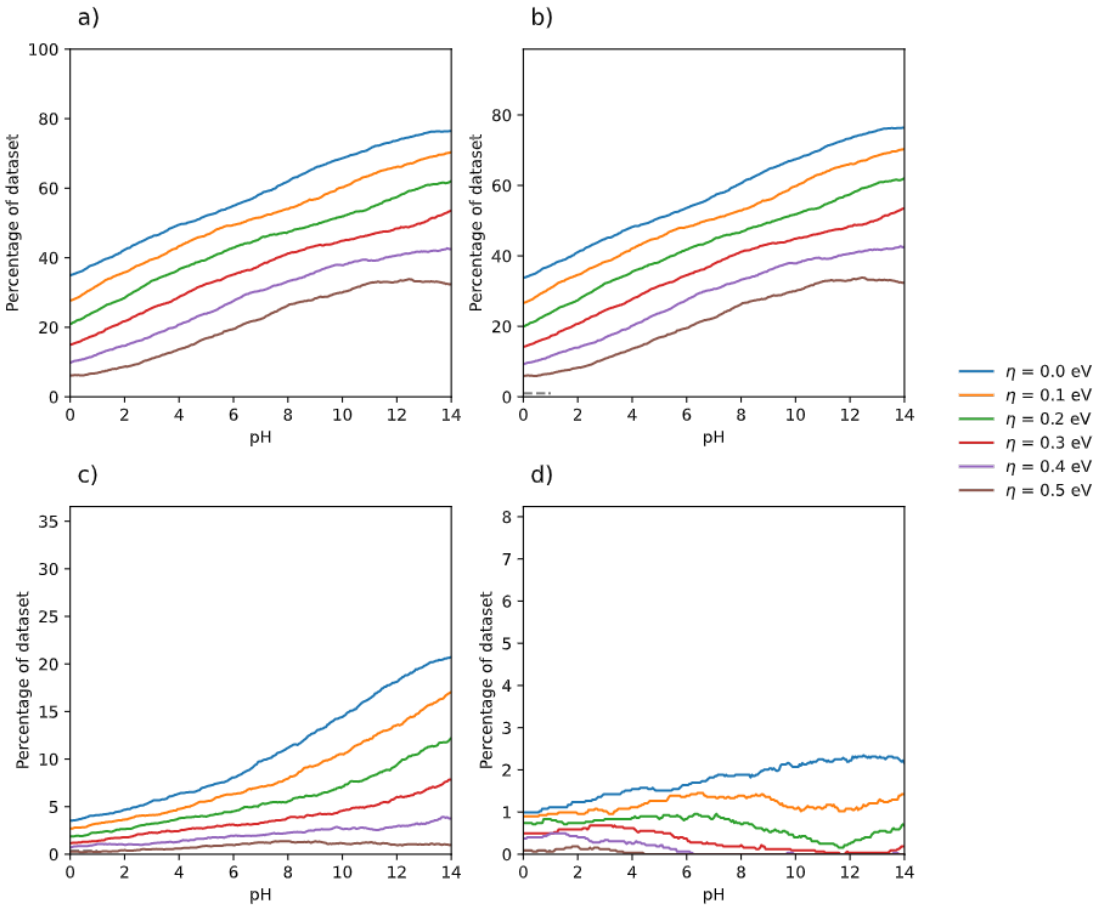

Fig. S3 *Percentage of (co-)polymers in the dataset that are predicted to be able to drive the overall splitting of water as a function of pH for different overpotential values and optical gap ranges. Panel a) includes all polymers predicted to have an optical gap between 0.0 and 3.5 eV, panel b) those with an optical gap between 1.23 eV and 3.5 eV, panel c) those with an optical gap between 1.23 eV and 2.5 eV, and 1.23 eV and 2.0 eV for panel d).*

Table S1 *Parameters of the linear model used to convert IPEA/sTDA-xTB values to the "DFT Scale".*

	EA	IP	Optical gap
Slope	0.84	0.88	0.85
Intercept	-0.75	-0.24	-0.25

Z-score analysis for water splitting under alkaline and acidic conditions

At acidic pH, the monomer with the highest z-score for both optical gap ranges is 3,6-coupled 1,2,4,5-tetrazine (D2, see figure 1C in the main text). This monomer occurs in 15 out of the 16 (< 2.0 eV) and 15 out of the 38 (< 2.5 eV) co-polymers that can drive overall water splitting at pH 0, respectively. For polymers with an optical gap below 2.5 eV several other monomers in the same neutral to acidic pH range also have relatively high z-scores: 1,4-coupled phthalazine (I2, occurring in 9 of the 38 co-polymers at pH 0) and 1,4-coupled 2,3,5,6-tetranitrobenzene (C1, occurring in 8 of the 38 co-polymers at pH 0), see figure 4a in the main text. In contrast, as can be seen in figure 4b in the main text, no other monomers than D2 have high z-scores at acidic pH when we limit the optical gap to 2.0 eV. For D2, I2 and C1 the z-scores increase with decreasing pH, in line with the fact that these are all electron poor monomers that are likely to result in co-polymers with deep, very positive, IP values, and the fact that at low pH polymers are most likely limited by their ability to oxidise water. At high pH, for polymers with an optical gap below 2.0 eV, 2,5-coupled furan (C4) and 5,8-coupled 1,6-naphthyridine (H8), as well as 2,5-coupled furo[3,2-*b*]furan (D4), have the highest z-scores, see figure 4b in the main text. At these pH values, > pH 12, water oxidation is thermodynamically easier relative to at low pH, explaining why some of these monomers are relatively electron rich (C4, D4). The overrepresentation of these monomers at alkaline pH values probably arises from the fact that co-polymers containing them have low(er) optical gaps rather than a deep IP. However, one should be careful not to overinterpret this data as the high z-scores in this region arise in part because very few polymers are predicted to have an optical gap < 2.0 eV and able to drive overall water splitting, specifically 6 polymers at pH 14, 3 of which contain D4 and 2 containing C4 or H8.

Based on the analysis above D2 is a promising monomer for polymers that can split water at acidic pH: 15 out of the 80 (co-)polymers in the dataset containing D2 (19%) are predicted to have an optical gap < 2.0 eV and to be able to drive overall water splitting under these conditions. However, as discussed in the methodology section in the main text, we do not consider the effect or protonation of nitrogen groups in the polymers in our screening, and such protonation probably will happen for polymers containing D2 under acidic conditions. Taking this into account, co-monomers leads for Susuki coupling of D2 include 1,4-dibromo-2-nitrobenzene (A8), 2,5-dibromoterephthalonitrile (B2), 2,5-dibromopyrimidine (C8), 2,5-dibromopyrazine (D1), 4,7-dibromobenzo[*c*][1,2,5]oxadiazole (E3), 2,7-dibromo-9*H*-fluoren-9-one (J5), and 3,7-dibromodibenzo[*b*,*d*]thiophene-5,5-dioxide (J8).