

Electronic Supplementary Information

Solar Energy Driven C–C Bond Cleavage in a Lignin Model Compound with a D– π –A Organic Dye-Sensitized Photoanode

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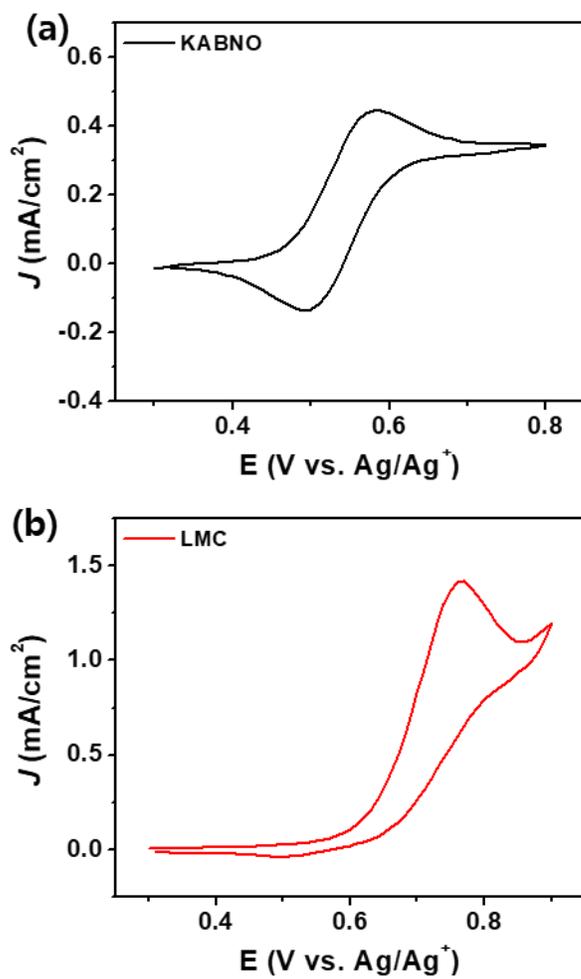


Fig. S1 CVs of (a) 3 mM **KABNO**, and (b) 3 mM **LMC** in 0.1 M TBAPF₆ acetonitrile. The experiment was performed using a glassy carbon working electrode, Pt counter electrode, and Ag/Ag⁺ reference electrode in the dark.

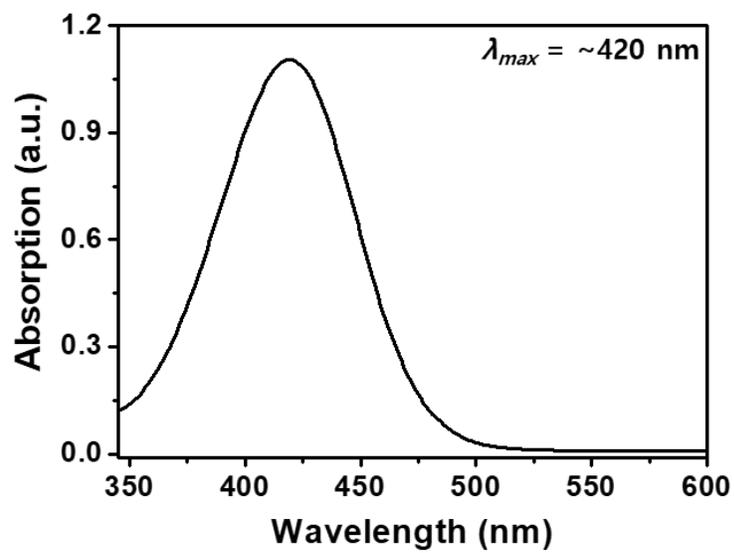


Fig. S2 UV-vis absorption of **DPTC** in ethanol solution.

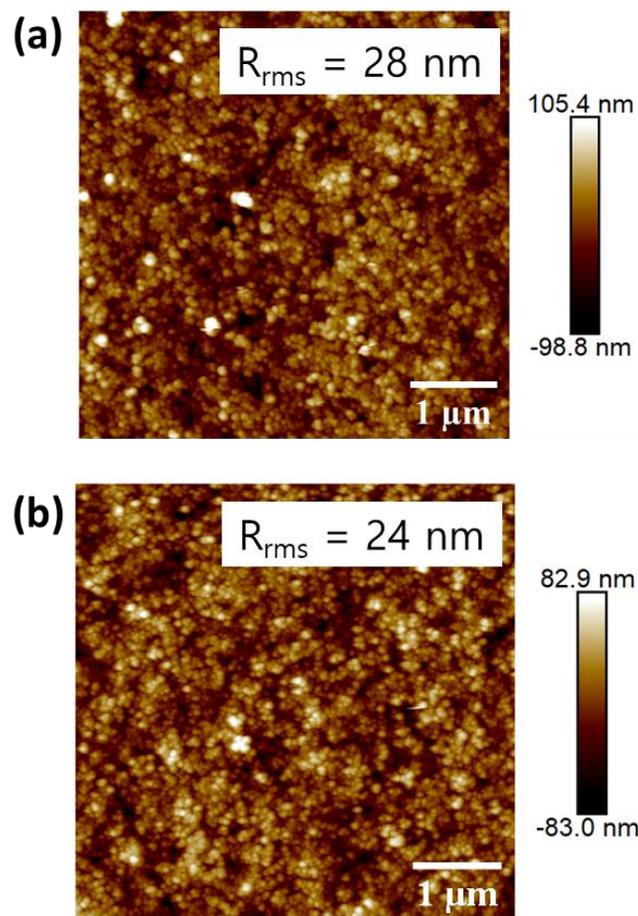


Fig. S3 AFM images of (a) bare FTO/TiO₂ and (b) FTO/TiO₂/DPTC. (Inset: R_{rms} is root mean square.)

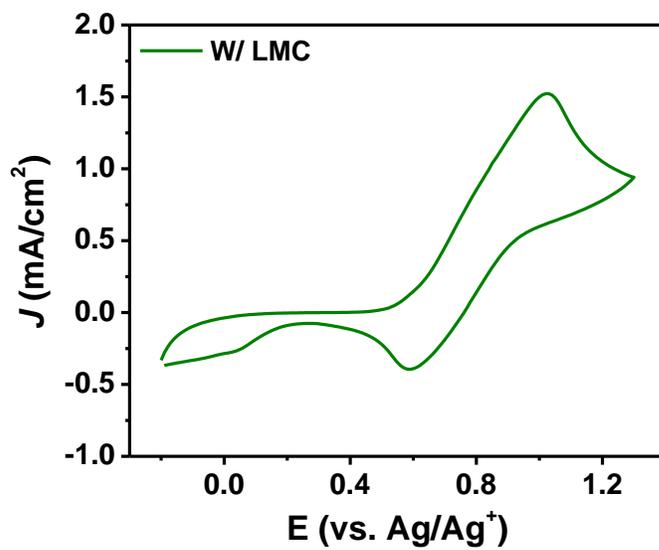


Fig. S4 CV of FTO/TiO₂/DPTC with 3 mM LMC in 0.1 M TBAPF₆ acetonitrile.

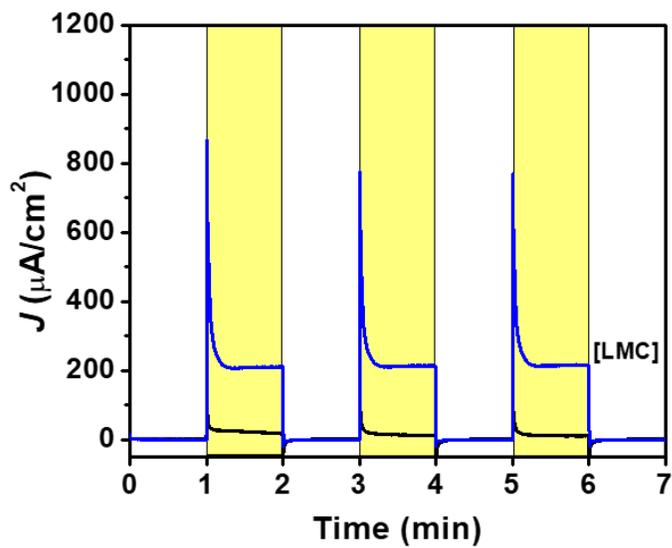


Fig. S5 Photocurrent-time traces of FTO/TiO₂/DPTC without (black) and with 3.0 mM LMC (blue).

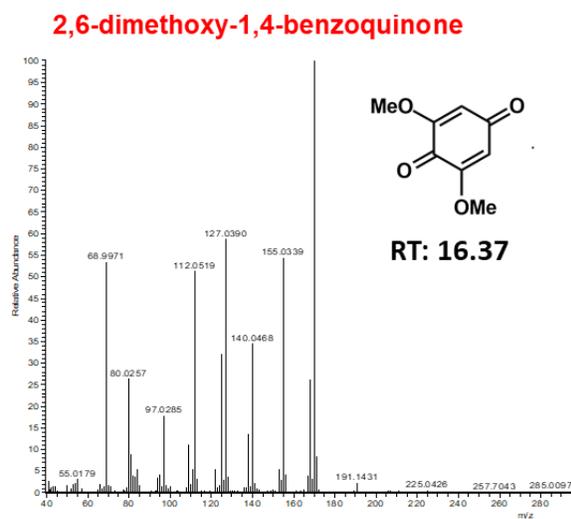
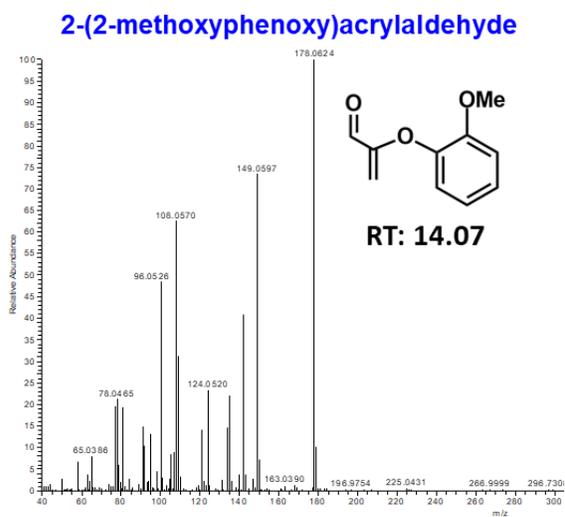


Fig. S6 Gas chromatography-mass spectra of **A** and **B** products after 24 h illumination.

The detailed $^1\text{H}/^{13}\text{C}$ NMR information of products A and B is provided. These peak assignments are consistent with the cleavage products from the previous studies.^{1,2}

Product **A** (Blue): 2-(2-methoxyphenoxy)acrylaldehyde. ^1H -NMR: δ 9.46 (s, 1H), 7.20-6.93 (m, 4H, aryl), 5.27 (d, $J = 2.8$ Hz, 1H), 5.08 (d, $J = 2.8$ Hz, 1H), 3.83 (s, 3H). ^{13}C -NMR: δ 186.98 (s), 158.20 (s), 151.17 (s), 142.85 (s), 126.28 (s), 122.11 (s), 121.21 (s), 113.13 (s), 107.26 (s), 55.89(s).

Product **B** (Red): 2,6-dimethoxy-1,4-benzoquinone. ^1H -NMR: δ 5.87 (s, 2H), 3.83 (s, 6H). ^{13}C -NMR: δ 186.84(s), 176.64 (s), 157.36(s), 107.41(s), 56.46(s).

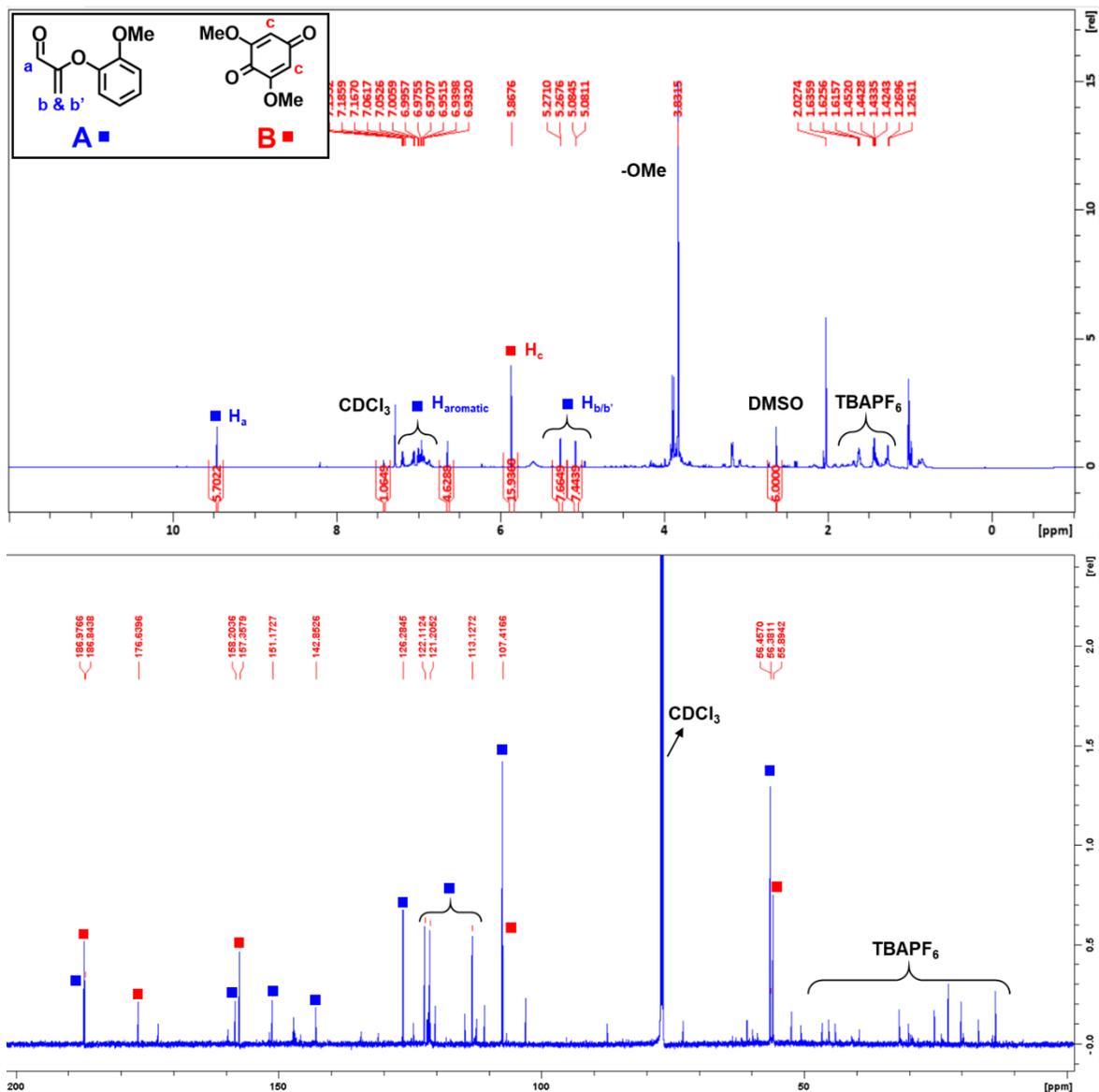


Fig. S7 ^1H -NMR (top) and ^{13}C -NMR (bottom) of reaction solution after 24 h illumination with DMSO as an internal standard.

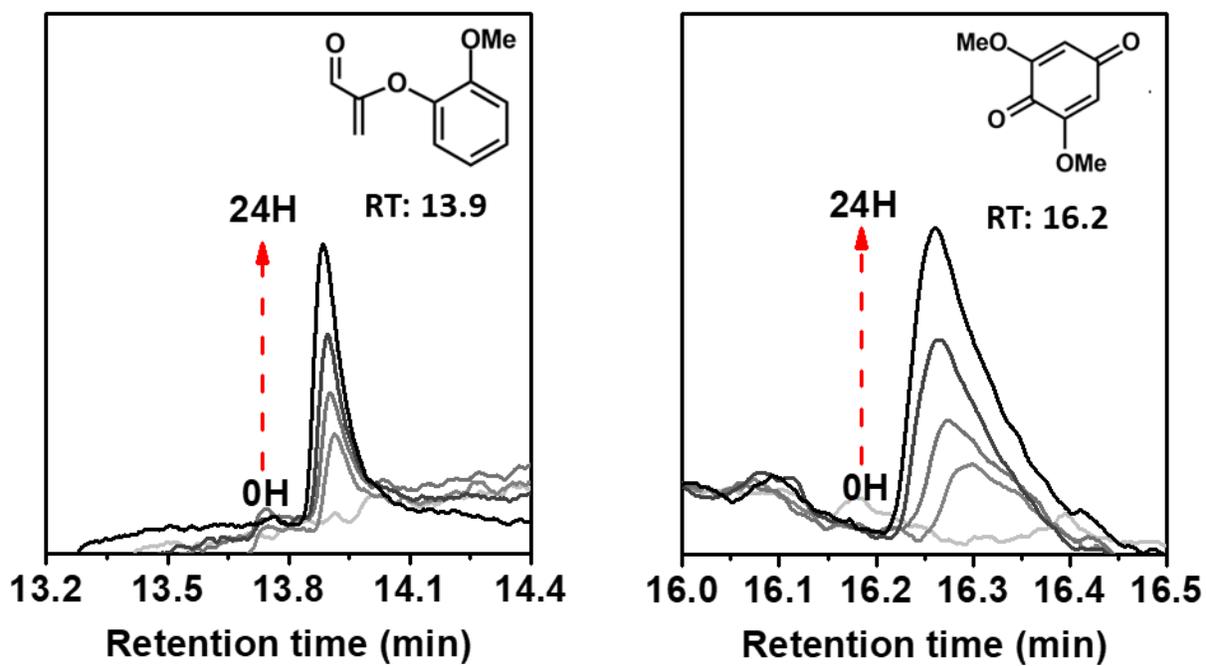
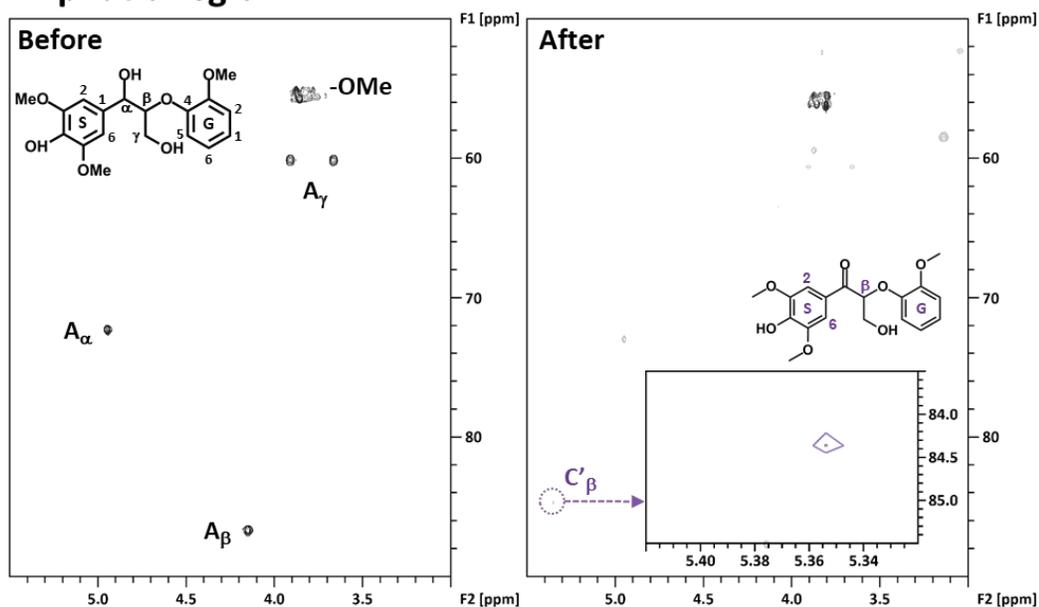


Fig. S8 GC-FID of cleavage products **A** and **B** in a DSPEC after 24 h illumination.

(a) Aliphatic Region



(b) Aromatic Region

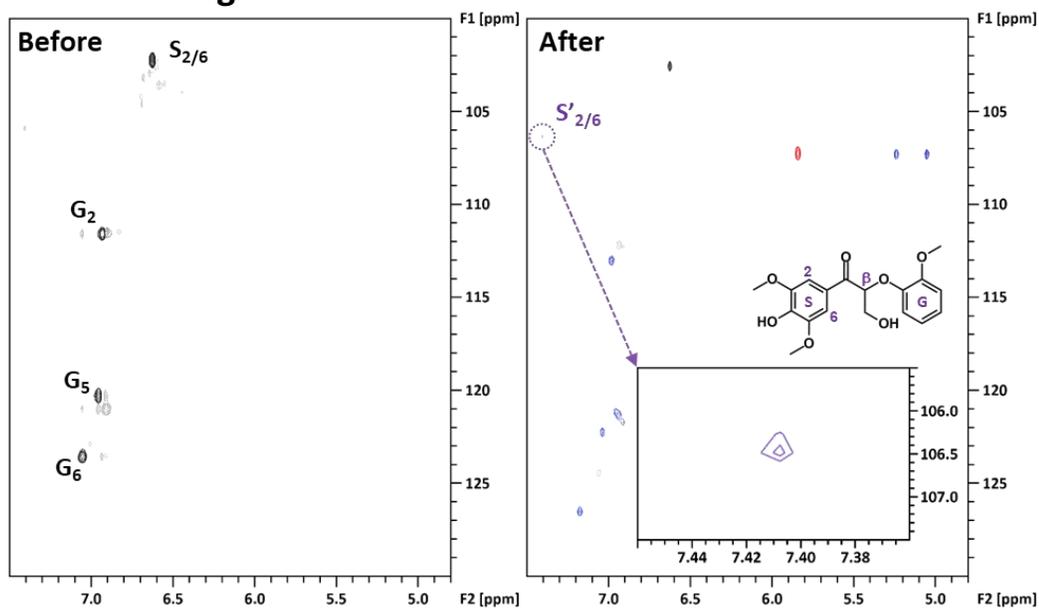


Fig. S9 2D HSQC NMR spectra of the oxidized LMC before (left) and after (right) the photoelectrolysis reaction: (a) aliphatic and (b) aromatic region.

References

1. S. Li, S. Kim, A. H. Davis, J. Zhuang, E. W. Shuler, D. Willinger, J.-J. Lee, W. Zheng, B. D. Sherman, C. G. Yoo and G. Leem, *ACS Catal.*, 2021, **11**, 3771–3781.
2. Y.-Y. Jiang, L. Yan, H.-Z. Yu, Q. Zhang, and Y. Fu, *ACS Catal.* 2016, **6**, 4399–4410.