Electronic Supplementary Information

Mechanistic analysis identifying reaction pathways for rapid reductive photodebromination of polybrominated diphenyl ethers using BiVO$_4$/BiOBr/Pd heterojunction nanocomposite photocatalyst

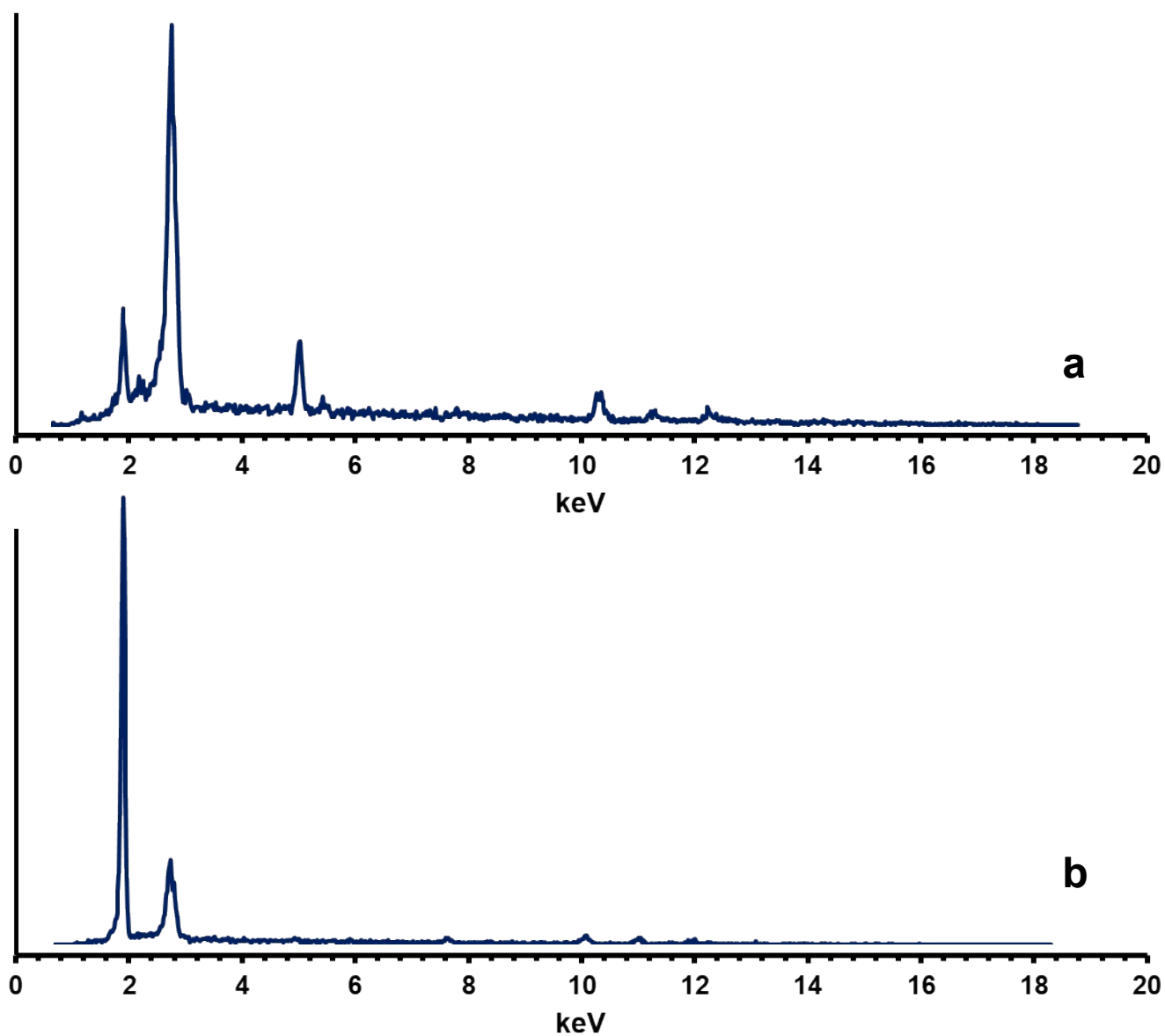Edward B. Miller,[a] Elsayed M. Zahran,[b] Marc R. Knecht,[a,c] and Leonidas G. Bachas[a,c]*

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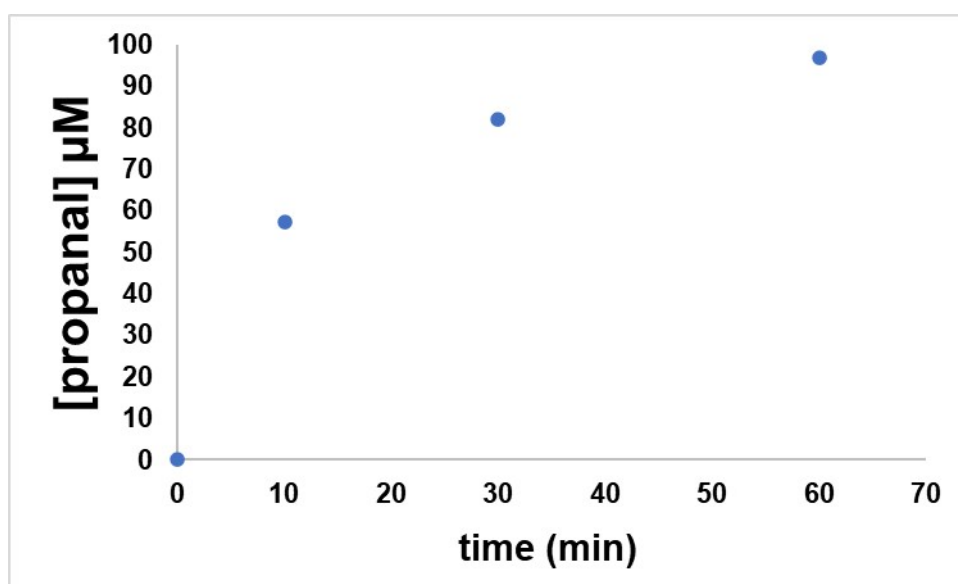
Contents

Figure S1. EDS spectra of (a) predominantly m-BiVO$_4$ region and (b) predominantly BiOBr region of the m-BiVO$_4$/BiOBr composite.
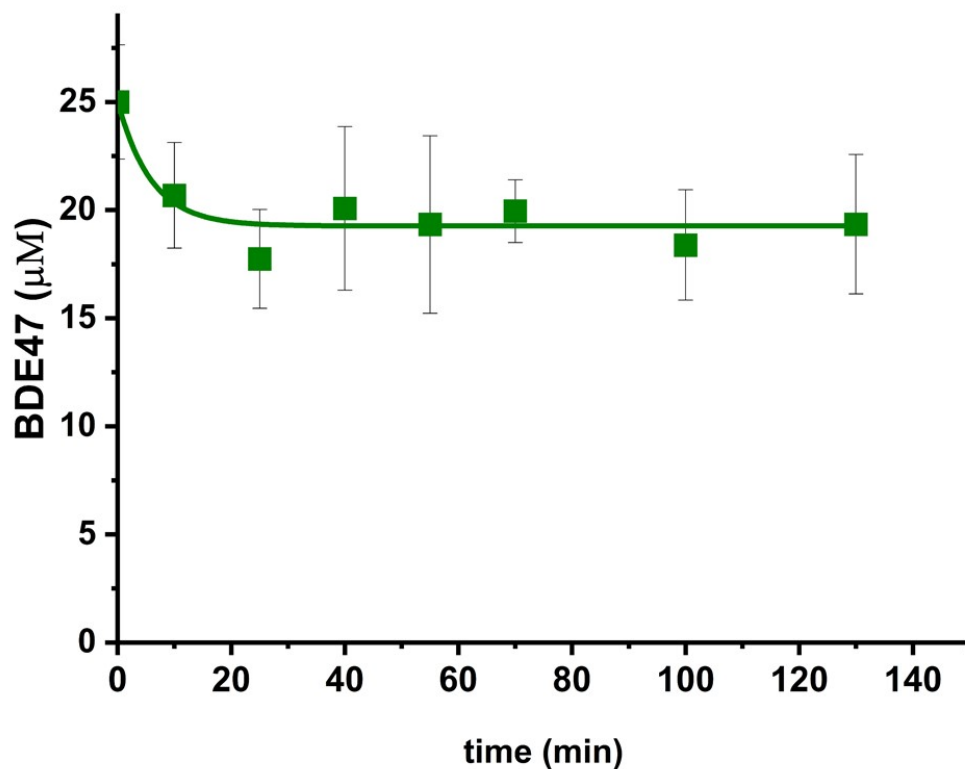
Figure S2. Adsorption of BDE-47 from 25 µM 1:1 EtOH/H_2O solution on $BiVO_4$/BiOBr/Pd particles stirring in darkness.

Figure S3. Propanal produced in the photodebromination of 100 µM BDE-3 with $BiVO_4$/BiOBr/Pd in 1:1 solution of 1-propanol / H_2O

Table S1. Reaction of BDE-3 with *m*-BiVO$_4$/BiOBr/Pd in different solvent systems
These reactions were done using a xenon lamp solar simulator as light source.

solvent system	reaction time		
	5 min	10 min	15 min
	Percent of initial BDE-3 concentration debrominated		
MeOH / H$_2$O (1:1)	80%	100%	100%
EtOH / H$_2$O (1:1)	80%	100%	100%
n-PrOH / H$_2$O (1:1)	45%	70%	75%
i-PrOH / H$_2$O (1:1)	NR	NR	NR *
t-BuOH / H$_2$O (1:1)	NR	NR	NR
ACN / H$_2$O (1:1)	NR	NR	NR
ACN / EtOH / H$_2$O (1:1:1)	25%	85%	100%

  * Trace amount of product detected after 30 min irradiation.

Natural Bond Orbital (NBO)[1] analysis of selected alcohols

In a search for some measure of theoretical insight, simple Density Functional Theory (DFT) calculations were performed for the C$_1$-C$_3$ alcohols in the gas phase, using the General Atomic and Molecular Electronic Structure System (GAMESS) package (US version),[2, 3] at the B3LYP/6-31G(d,p)[4-9] level of theory for geometry optimization, vibrational frequency, and single-point energy calculations. Initial (unoptimized) geometries, used for the input to GAMESS, were constructed using Avogadro (version 1.2.0).[10, 11] Conformations yielding the lowest total energy after optimization were used. Calculated energy, vibrational frequencies, and thermodynamic quantities were compared against the NIST Computational Chemistry Comparison and Benchmark Database[12] for validation of results. NBO analysis was completed in conjunction with the single-point energy calculations using NBO 7.0,[13] which was linked with the GAMESS package. Selected results are listed in Table S2. In addition, pK_a values[14] for the hydroxyl H atoms are included for reference.

Table S2. Select computed Natural Bond Orbital (NBO) data for C1-C3 alcohols, from DFT calculations at the B3LYP/6-31G(d,p) level.

Interactions greater than 20 kJ/mol for donor-acceptor pairs are listed. Dissociation constants (pK_a) for the alcohols included for reference.

alcohol	pK_a[14]	natural charge on α-H			donor-acceptor orbital interactions (kJ/mol)					
methanol	15.09	0.19003	0.19003	0.21676	O$_{l.p.}$	σ* C-H$_{\alpha1}$	26.6	O$_{l.p.}$	σ* C-H$_{\alpha2}$	26.6
ethanol	15.93	0.19518	0.19531		O$_{l.p.}$	σ* C-H$_{\alpha1}$	25.6	O$_{l.p.}$	σ* C-H$_{\alpha2}$	25.4
1-propanol	16.1	0.19284	0.21869		O$_{l.p.}$	σ* C-H$_{\alpha1}$	24.0	O$_{l.p.}$	σ* C$_1$-C$_2$	27.9
2-propanol	17.1	0.23011			O$_{l.p.}$	σ* C$_1$-C$_2$	25.3	O$_{l.p.}$	σ* C$_1$-C$_3$	25.2

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