Supporting Information

Photophysics of Perylene Diimide Dianions and Their Application in Photoredox Catalysis
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# Supporting Information

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1. Materials and instrumentation

All reagents for synthesis are commercial quality. Unless otherwise indicated, the chemicals used for optical spectroscopy, electrochemistry, and preparative photo-irradiation experiments were purchased from commercial suppliers in high purity and were used as received. The solvents for electrochemical and photochemical experiments were DMF (99.8 %, Sigma-Aldrich) and ultrapure Millipore MilliQ water (specific resistance, 18.2 MΩ cm). The pH values were adjusted either with sodium hydroxide or with a freshly prepared phosphate buffer.

The samples for UV-Vis absorption and photoluminescence in DMF were prepared in a glovebox (LABStar ECO from MBRAUN company), and a solution of the chemical reductant in DMF was added with a Hamilton syringe. The cuvettes containing the mixture of PDI sample and chemical reductant were sealed with septum caps and then taken out of the glovebox. The solutions for UV-Vis absorption and steady-state luminescence measurements in ultrapure water were purged with argon for at least 5 minutes before the measurements and sealed under inert gas (1 atm) using cuvettes with septum caps. NaOH (> 98 %, Sigma-Aldrich) was added to the aqueous solutions (final NaOH concentration: 50 mM) to ensure (i) a quasi-constant ionic strength, and (ii) fast dissolution of the Na$_2$S$_2$O$_4$ reductant, and (iii) to preclude protonation of PDI dianions. The PDI solutions for laser flash photolysis in ultrapure water were deaerated using at least three freeze-pump-thaw cycles with argon, and were then added to sealed cuvettes equipped with septum caps, which contained the Na$_2$S$_2$O$_4$ reductant under argon.

NMR spectroscopy was performed with Bruker Avance III systems operating at 400 MHz or 500 MHz proton frequencies, using deuterated solvents with TMS as an internal standard. All chemical shifts are reported in ppm values and are referenced to the signals of the residual non-perdeuterated solvent used.$^{[1]}$ $^{19}$F-NMR spectra were referenced to trifluoroacetic acid (TFA, −75.3 ppm).$^{[2]}$ Deuterated solvents were obtained from Cambridge Isotope Laboratories. All coupling constants J are given in Hertz (Hz) and the following abbreviations are used to describe their coupling patterns: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and combinations of these abbreviations.

ESI mass spectra were recorded on a Di-ESI-MS 8030 Plus instrument (Shimadzu). High resolution mass spectrometry was recorded with the help of Dr. Michael Pfeffer on a Bruker maXis 4G QTOF ESI spectrometer.

Elemental analyses were carried out by Ms. Sylvie Mittelheisser on a Vario Micro Cube instrument in the Department of Chemistry at the University of Basel.

Steady-state absorption and luminescence spectra were recorded using a Cary 5000 spectrophotometer (Varian) and a Fluorolog-3-22 instrument (Horiba Jobin-Yvon), respectively.

Emission lifetime and quenching investigations were carried out with a LifeSpec II setup (Edinburgh Instruments), operating on the basis of time-correlated single photon counting (TCSPC) technique. A picosecond pulsed diode laser (ca. 75 ps pulse width) was used for excitation of PDI and PDI$^{2−}$ at 472.8 nm. The PDI and PDI$^{2−}$ concentrations for these lifetime measurements were between 40 and 60 μM.

For the electrochemical measurements, a three-electrode system connected to a VersaSTAT 3-200 potentiostat from Princeton Applied Research was used for the measurement in aqueous solution outside the glovebox, and a system connected to a VersaSTAT 4-200 potentiostat from Princeton Applied Research was employed for the measurements in DMF inside the glovebox. The cyclic voltammograms obtained in DMF or THF were carried out inside the glovebox, whereas the CVs in water were measured outside the glovebox under argon. A glassy carbon electrode (GC) served as the working electrode, and a Pt wire was employed as counter electrode. For measurements in DMF, a silver wire served
as quasi-reference electrode, whilst for measurements in aqueous solution a saturated calomel electrode (SCE) was used as reference electrode. For measurements in DMF, ferrocene was added as an internal reference. Voltage scans were performed at rates of 100 mV/s. The supporting electrolyte was 0.1 M tetra-\textit{n}-butylammonium hexafluorophosphate (TBAPF$_6$) solution in DMF and 0.1 M pH = 7 phosphate buffer (PBS) in water, respectively. The transient absorption spectroscopy was recorded on an LP920-KS instrument from Edinburgh Instruments. Excitation of PDI(H)-PEG$^2-$ at 532 nm occurred with the frequency-doubled output of a Nd:YAG laser (Quantel Brilliant b, ca. 10 ns pulse width, 10 Hz pulse frequency). The typical pulse energy used for transient absorption studies was around 10 mJ. Transient absorption spectra were detected with an iCCD camera from Andor, and single-wavelength kinetics were recorded with a photomultiplier tube. All spectroscopic experiments were carried out at 293 K using cuvette holders allowing temperature control.
2. Synthesis and product characterization

**PEG₇-OTs:**

\[
\begin{align*}
\text{H}_3\text{C(O)}\left(\overset{\text{7}}{\text{O}}\right)\text{OH} & \quad \text{DCM} \quad \text{Pyridine} \\
& \quad 25^\circ\text{C}, \text{N}_2 \\
& \quad \text{PEG} \quad \text{OTs} \\
\end{align*}
\]

\(p\)-Toluenesulfonyl chloride (715.4 mg, 3.75 mmol) and methoxypolyethylene glycol (\(M_w = 350, 878.5 \text{ mg, 2.5 mmol}\)) were dissolved in dry DCM (12 mL) under Ar. 1 mL pyridine (0.6 mL, 3 mmol) was added under Ar at room temperature, and the mixture was stirred at room temperature for ca. 19.5 hours. The mixture was treated with 0.5 M aqueous HCl and water, then was extracted with DCM. The combined organic phases were dried over anhydrous Na₂SO₄. After filtration, the solvent was removed on a rotary evaporator, and the crude product was purified by column chromatography (silica gel) using ethyl acetate / petroleum ether (1/2 to 3/1, v/v) as eluent to yield **PEG₇-OTs** as a colorless liquid (722.6 mg, yield 58%).

\(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) (ppm): 7.80 (d, \(J = 8.2 \text{ Hz, 2H}\)), 7.34 (d, \(J = 8.0 \text{ Hz, 2H}\)), 4.17 – 4.15 (t, 2H), 3.71 – 3.53 (m, 26H), 3.38 (s, 3H), 2.45 (s, 3H).

\(^{13}\)C NMR (126 MHz, CDCl₃) \(\delta\) (ppm): 129.83, 128.00, 71.95, 70.77, 70.63, 70.59, 70.53, 69.24, 68.70, 59.04, 21.65.

**PEG₇-N₃:**

\[
\begin{align*}
\text{H}_3\text{C(O)}\left(\overset{\text{7}}{\text{O}}\right)\text{OTs} & \quad \text{EtOH} \\
& \quad 78^\circ\text{C} \\
& \quad \text{PEG} \quad \text{N}_3 \\
\end{align*}
\]

A solution of **PEG₇-OTs** (722.6 mg, 1.46 mmol) and sodium azide (121.1 mg, 1.86 mmol) in 10 mL of EtOH was heated to reflux overnight. After cooling to room temperature, 25 mL of water was added and the mixture was extracted with DCM. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was evaporated. A slightly yellow oil (**PEG₇-N₃**) was obtained without further purification (524.2 mg, yield 98%).

\(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) (ppm): 3.70 – 3.60 (m, 24H), 3.55 (dd, \(J = 5.7, 3.6 \text{ Hz, 2H}\)), 3.49 – 3.27 (m, 5H).

\(^{13}\)C NMR (126 MHz, CDCl₃) \(\delta\) (ppm): 129.86, 128.00, 71.95, 70.77, 70.63, 70.59, 70.53, 69.24, 68.70, 59.05, 50.71.
PEG\(_7\)-N\(_3\) (524.4 mg, 1.44 mmol) was dissolved in dry Et\(_2\)O (15 mL). This solution was then slowly added to 1 M LiAlH\(_4\) solution in THF (3 mL) under N\(_2\). The reaction mixture was stirred for 2 h at room temperature under N\(_2\), then it was then cooled to 0 °C, and the excess LiAlH\(_4\) was quenched with MeOH. The mixture was then partitioned between Et\(_2\)O and water containing brine, and the aqueous phase was further extracted with DCM. The combined organic phases were dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated under vacuum to get PEG\(_7\)-NH\(_2\) as colorless oil (441.6 mg, yield 90%).

\[^1\]H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 3.66 – 3.51 (m, 24H), 3.54 (ddd, \(J = 16.4, 7.7, 4.1\) Hz, 4H), 3.38 (s, 3H), 2.87 (t, \(J = 5.2\) Hz, 2H).

\[^1\]C NMR (126 MHz, CDCl\(_3\)) \(\delta\) (ppm): 73.49, 71.96, 70.59, 70.54, 70.32, 59.05, 41.85.

PDI(H)-PEG\[^6\]

To 3,4,9,10-perylenetetracarboxy dianhydride (PDA, 123.4 mg, 0.31 mmol) was added PEG\(_7\)-NH\(_2\) (213 mg, 0.63 mmol) and Zn(OAc)\(_2\) (26.2 mg, 0.14 mmol) and imidazole (1.269 g, 18.67 mmol). The reaction mixture was heated to 160 °C under N\(_2\). After 18 h, the mixture was cooled to room temperature and 10 mL EtOH and 12 mL 2 M aqueous HCl solution were added. This mixture was stirred for 0.5 h and then filtered. Then, the mixture was extracted with DCM and the organic layer was collected. The organic phase was dried with anhydrous Na\(_2\)SO\(_4\). The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography (silica gel; eluent: DCM/MeOH = 20/1, v/v) to afford PDI(H)-PEG as a red-brown solid (250.4 mg, yield 78%).

\[^1\]H NMR (500 MHz, CDCl\(_3\)) \(\delta\) (ppm): 8.67 (d, \(J = 7.9\) Hz, 4H), 8.60 (d, \(J = 7.8\) Hz, 4H), 4.47 (t, \(J = 6.1\) Hz, 4H), 3.87 (t, \(J = 6.1\) Hz, 4H), 3.76 – 3.71 (m, 4H), 3.69 – 3.56 (m, 40H), 3.56 – 3.51 (m, 4H), 3.42 – 3.33 (m, 6H).

\[^1\]C NMR (126 MHz, CDCl\(_3\)) \(\delta\) (ppm): 163.18, 134.23, 131.19, 123.08, 122.98, 71.93, 70.57, 70.11 (s), 67.90, 59.03, 39.32.

ESI-MS \(m/z\): [M+Na]\(^+\): Calculated: 1057.4521; Experiment: 1057.4515 (main peak for PEG chain length of 7).

[M\(^-\)–CH\(_2\)CH\(_2\)O+2Na]\(^2+\): Calculated: 606.2603; Experiment: 606.2593 (peak for PEG chain length of 9).

[M+2Na]\(^2+\): Calculated: 540.2210; Experiment: 540.2205.

Elemental analysis: calcd. for C\(_{54}\)H\(_{70}\)N\(_2\)O\(_{18}\)•2H\(_2\)O•CH\(_3\)OH: Calculated: C, 59.88; H, 7.13; N, 2.54; Experiment: C, 59.92; H, 7.234; N, 2.51.
To 3,4,9,10-perylenetetracarboxy dianhydride (PDA, 98.2 mg, 0.25 mmol) was added 2,6-diisopropylaniline (0.35 mL, 1.86 mmol) and imidazole (736 mg, 10.8 mmol). The reaction mixture was heated to 190 °C under N₂. After 24 h, the mixture was cooled to room temperature and 10 mL EtOH and 12 mL 2 M aqueous HCl solution were added. This mixture was stirred for 3 h and then filtered. The solvent was evaporated on a rotary evaporator. The dark red material was purified by column chromatography (silica gel; eluent DCM/MeOH = 100/1, v/v) to yield PDI(H)-dipp (35.9 mg, yield 20%).

\(^1\)H NMR (400 MHz, CDCl₃) δ (ppm): 8.82 – 8.73 (m, 8H), 7.51 (t, J = 7.7 Hz, 2H), 7.36 (d, J = 7.8 Hz, 4H), 2.82 – 2.70 (m, 4H), 1.19 (d, J = 6.9 Hz, 24H).

\(^{13}\)C NMR (126 MHz, CDCl₃) δ (ppm): 163.49, 145.66, 135.09, 132.11, 130.53, 130.20, 129.72, 128.09, 126.87, 125.04, 124.87, 124.14, 123.44, 123.35, 34.17, 29.24, 28.77, 24.02, 23.77.

ESI-MS (m/z): [M+H]⁺: Calculated: 711.3217; Experiment: 711.3208.

Elemental analysis: calcd. for C₄₈H₄₂N₂O₄•1.5H₂O: Calculated: C, 78.13; H, 6.15; N, 3.80; Experiment: C, 78.36; H, 6.13; N, 3.98.

PDA-Br:[⁸]

A mixture of 3,4:9,10-perylenetetracarboxy dianhydride (PDA, 588.8 mg, 1.50 mmol) and 12 mL 95 wt% sulfuric acid was stirred for 2 h at room temperature, and subsequently I₂ (15.5 mg, 0.062 mmol) was added. The reaction mixture was heated to 85 °C, and bromine (0.25 mL, 777.5 mg, 4.87 mmol) was added dropwise. After bromine addition, the reaction mixture was heated for an additional 10 h at 100 °C and finally it was cooled to room temperature by adding ice. The resulting precipitate was then filtered and washed first with an aqueous solution of 5% sodium metabisulfite to eliminate the residual bromine, and then several times with neat water. The solid was then dried at 120 °C in an oven. The red solid PDA-Br (784.5 mg, yield 95%) thus obtained had a sufficient degree of purity to be used for the next steps without further purification.

\(^1\)H NMR (400 MHz, DMSO-d₆) δ (ppm): 9.51 (t, J = 7.6 Hz, 2H), 8.79 (d, J = 8.5 Hz, 2H), 8.72 – 8.67 (m, 2H).
A suspension of brominated perylene bisanhydride (PDA-Br, 134.9 mg, 0.25 mmol) and excess PEG₇-NH₂ (213.2 mg, 0.63 mmol) in 10 mL propionic acid under N₂ atmosphere was stirred and heated to 120 °C overnight. After cooling to room temperature, the resulting solution was poured into 20 mL of water. The red solid was collected, then redissolved in DCM, washed with water and brine until neutral, and then dried over anhydrous Na₂SO₄. After removing the solvent, the crude product was purified by silica gel column chromatography (eluent: DCM/petroleum ether = 5/1 to DCM/MeOH = 20/1 in v/v) to obtain PDI(Br)-PEG as an orange-red solid (29.8 mg, yield 10%).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 9.47 (d, J = 8.1 Hz, 2H), 8.90 (s, 2H), 8.69 (d, J = 8.2 Hz, 2H), 4.46 (t, J = 5.9 Hz, 4H), 3.85 (t, J = 5.7 Hz, 4H), 3.76 – 3.49 (m, 48H), 3.36 (d, J = 7.8 Hz, 6H).

¹³C NMR (126 MHz, CDCl₃) δ (ppm): 162.86, 162.38, 138.00, 132.98, 132.81, 130.05, 129.20, 128.50, 126.96, 123.08, 122.65, 122.36, 121.63, 120.80, 71.93, 70.56, 70.51, 70.14, 67.83, 59.03, 39.47.

ESI-MS (m/z): [M–CH₂CH₂O+Na]⁺: Calculated: 1171.2449 (⁷⁹Br₅¹Br); Experiment: 1171.2448 (⁷⁹Br₅¹Br)

[M+Na⁺]: Calculated: 1215.2711 (⁷⁹Br₅¹Br); Experiment: 1215.2709 (⁷⁹Br₅¹Br) (main peaks for PEG chain length of 7).

[M'–CH₂CH₂O+2Na]^⁺: Calculated: 685.1698 (⁷⁹Br₅¹Br); Experiment: 685.1695 (⁷⁹Br₅¹Br) (peak for PEG chain length of 9).

Elemental Analysis: calcd. for C₅₄H₆₈Br₂N₂O₁₈•2CH₂Cl₂: Calculated: C, 51.70; H, 5.52; N, 2.19; Experiment: C, 51.76; H, 5.33; N, 2.19.
A suspension of brominated perylene bisanhydride (PDA-Br, 135.6 mg, 0.25 mmol) and excess 2,6-diisopropylaniline (0.15 mL, 0.80 mmol) in 5 mL propionic acid under N$_2$ atmosphere was stirred and heated to 120 ºC for 4 days. After cooling to room temperature, the resulting solution was poured into 20 mL of water. The red solid was collected, washed with water and brine until neutral and dried under vacuum. The crude product was purified by column chromatography (silica gel; eluent: DCM/petroleum ether = 1/2 to 5/1 in v/v). The PDI(Br)-dipp target compound was obtained as a red solid (95.3 mg, yield 44%).

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 9.57 (d, $J = 8.1$ Hz, 2H), 9.03 (s, 2H), 8.81 (d, $J = 8.1$ Hz, 2H), 7.52 (t, $J = 7.8$ Hz, 2H), 7.37 (d, $J = 7.8$ Hz, 4H), 2.81 – 2.67 (m, 4H), 1.19 (d, $J = 6.8$ Hz, 24H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ (ppm): 163.00, 162.51, 145.61, 138.48, 133.28, 130.65, 130.13, 129.91, 129.64, 128.73, 124.22, 123.21, 122.88, 121.07, 29.30, 24.04, 24.01.

ESI-MS (m/z): [M+H]$^+$: Calculated: 867.1428 ($^{79}$Br$^{79}$Br), 869.1407 ($^{80}$Br$^{80}$Br), 871.1441 ($^{81}$Br$^{81}$Br); Experiment: 867.1429 ($^{79}$Br$^{79}$Br), 869.1398 ($^{80}$Br$^{80}$Br), 871.1396 ($^{81}$Br$^{81}$Br).

Elemental analysis: calcld. for C$_{48}$H$_{40}$Br$_2$N$_2$O$_4$$\cdot$1.5H$_2$O: Calculated: C, 64.37; H, 4.84; N, 3.13; Experiment: C, 64.67; H, 5.04; N, 2.99.

Precursor for the OED:[11]

A solution of 4-(dimethylamino)pyridine (1.33 g, 10.89 mmol, 2.5 eq.) and 1,3-diiodopropane (0.5 mL, 1.288 g, 4.35 mmol, 1 eq.) in acetonitrile (15 mL) was stirred at reflux under argon overnight. After cooling, the solid that had appeared was filtered. This solid was washed with acetonitrile (3 × 20 mL) and with diethyl ether (3 × 20 mL) and dried under vacuum to afford 1,3-bis(N′, N′-dimethyl-4-aminopyridinium)propane diiodide as a white solid (2.146 g, yield 91%).

$^1$H NMR (400 MHz, DMSO) δ (ppm): 8.28 (d, $J = 7.7$ Hz, 4H), 7.06 (d, $J = 7.7$ Hz, 4H), 4.24 (t, $J = 7.2$ Hz, 4H), 3.20 (s, 12H), 2.39 – 2.30 (m, 2H).

$^{13}$C NMR (126 MHz, DMSO) δ (ppm): 155.88, 141.93, 107.80, 53.80, 39.53, 31.02.
For optical spectroscopic measurements, chemical reductants were employed to form PDI\(^{-}\) and PDI\(^{2-}\) species in situ from charge-neutral PDI precursor compounds (Scheme S1). In DMF, a very strong organic electron donor (OED) was formed from a suitable precursor molecule (upper right corner in Scheme S1, see section 1 for its synthesis\[^{[12]}\] and NaH, whereas in aqueous solution Na\(_2\)S\(_2\)O\(_4\) was employed as reductant.\[^{[13]}\]

**Figure S1.** Chemical reduction of the charge-neutral PDI units to their dianion forms in DMF (a) and in aqueous solution (b).
Lignin model substrate 4; 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethenone\[14\]

![Reaction scheme](image)

A mixture comprised of 2-bromo-1-(4-methoxyphenyl)ethanone (574.5 mg, 2.51 mmol), potassium carbonate (516.8 mg, 3.74 mmol), guaiacol (0.30 mL, 2.72 mmol), and acetone (20 mL) was stirred and heated to reflux for 3 h. After filtration through celite the solvent was evaporated, and the resulting solid was purified by chromatography on silica gel (petroleum ether/EtOAc = 7/3, v/v), yielding a colorless solid (526.7 mg, yield 77%).

\[1\]H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 8.06 – 7.99 (m, 2H), 6.99 – 6.90 (m, 4H), 6.88 – 6.83 (m, 2H), 5.28 (s, 2H), 3.88 (d, \(J = 3.9\) Hz, 6H).

\[13\]C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 193.16, 163.97, 149.77, 147.65, 130.54, 127.76, 122.34, 120.81, 114.76, 113.96, 112.19, 72.03, 55.94, 55.52.

Lignin model substrate 5; benzyl formate: commercially available.

Lignin model substrate 6; 2-(4-methoxyphenyl)-2-oxoethyl acetate\[14a, 15\]

To a suspension of 2-bromo-1-(4-methoxyphenyl)ethanone (584.1 mg, 2.55 mmol) in 10 mL of ethanol a solution of sodium acetate (240.5 mg, 2.93 mmol) in 5 mL of water, and 0.3 mL of acetic acid were added. The reaction mixture was refluxed for 2.5 h, then cooled to room temperature, and kept in the refrigerator overnight. Solid that separated (acetate) was collected by filtration. Most of the ethanol was removed under reduced pressure, and the resulting oily mixture was distributed between 30 mL EtOAc and 20 mL of an ice-cold NaHCO\textsubscript{3} solution. The combined organic phases were washed with 10 mL of brine, dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, and evaporated in vacuo. Purification by chromatography on silica gel (petroleum ether/EtOAc = 7/3, v/v) gave the desired product as a colorless solid (522.4 mg, yield 98%).

\[1\]H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 7.90 (d, \(J = 8.9\) Hz, 2H), 6.95 (d, \(J = 8.9\) Hz, 2H), 5.30 (s, 2H), 3.88 (s, 3H), 2.23 (s, 3H).

\[13\]C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) (ppm) 190.60, 170.51, 164.07, 130.07, 127.26, 114.07, 65.77, 55.54, 20.63.
Lignin model substrate 7; 3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one:[16]

To a solution of 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone (407.0 mg, 1.50 mmol) in EtOH/acetone (v/v = 1/1, 20 mL) containing K₂CO₃ (230.4 mg, 1.67 mmol), formalin solution was added (37 wt.%, 227.4 mg, 2.80 mmol). The reaction mixture was stirred at r.t. for 2 h and then filtered. After washing with acetone and concentration in vacuo, the crude product was obtained as an orange-pink oil. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 4/1 ~ 1/1, v/v) afforded the desired product as pale-yellow oil (317.3 mg, yield 70%).

1H NMR (500 MHz, CDCl₃) δ (ppm) 8.14 – 8.01 (m, 2H), 7.00 (t, J = 7.7 Hz, 1H), 6.96 – 6.87 (m, 4H), 6.82 (t, J = 7.7 Hz, 1H), 5.37 (m, 1H), 4.05 (t, J = 5.6 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H), 3.07 (t, J = 6.2 Hz, 1H).

13C NMR (126 MHz, CDCl₃) δ (ppm) 195.00, 164.11, 150.60, 147.00, 131.31, 123.72, 121.17, 118.83, 113.98, 112.33, 84.85, 63.61, 55.83, 55.54.

4-Benzyl oxyacetophenone:[17]

To a solution of 4-hydroxyacetophenone (464.7 mg, 3.41 mmol) in DMF (5 mL) was added benzyl chloride (0.41 mL, 3.56 mmol) and K₂CO₃ (945.3 mg, 6.84 mmol). The mixture was reacted at 70 °C for 2 h, and reaction progress was monitored by TLC. After cooling to room temperature, the mixture was diluted with EtOH (30 mL) and poured slowly into rapidly stirring water (100 mL). The white precipitate was collected by filtration and washed with water (100 mL). The solid was dried overnight in vacuo to afford the desired product as a white solid (767.9 mg, yield: 95%)

1H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 8.8 Hz, 2H), 7.48 – 7.31 (m, 5H), 7.01 (d, J = 8.8 Hz, 2H), 5.14 (s, 2H), 2.56 (s, 3H).

13C NMR (126 MHz, CDCl₃) δ 196.76, 136.19, 130.61, 130.56, 128.71, 128.26, 127.48, 114.56, 70.15, 26.36.
4-Benzyl氧-α-bromoacetophenone:[17]

![Chemical structure of 4-benzyloxy-α-bromoacetophenone](image)

4-Benzyl氧acetophenone (403.7 mg, 1.78 mmol) was dissolved in a mixture of EtOH (15 mL) and dichloromethane (1.5 mL) while stirring under Argon. Br₂ (0.11 mL, 2.00 mmol) in cyclohexane (1.7 mL) was rapidly added to the stirred mixture under Argon at room temperature. Reaction progress was monitored by TLC (petroleum ether/ethyl acetate = 2/1, v/v). After 40 min of continuous stirring, reaction mixture was poured onto ice, and a white solid substance formed. This mixture was stirred until the ice was molten. The solid was collected by suction filtration, and then washed with water and hexane. The desired product was dried in vacuo to afford a pale yellow white solid (533.8 mg, yield 98%).

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta \ 7.97 \ (d, \ J = 8.9 \text{ Hz, 2H}), 7.48 - 7.33 \ (m, 5H), 7.04 \ (d, \ J = 8.9 \text{ Hz, 2H}), 5.15 \ (s, 2H), 4.40 \ (s, 2H). \]

\[ \text{C NMR (126 MHz, CDCl}_3\text{)} \delta 189.93, 163.29, 131.39, 128.76, 128.36, 127.50, 127.13, 114.92, 70.27, 30.66. \]

1-(4-(benzyloxy)phenyl)-2-(2-methoxyphenoxy)ethan-1-one:[14a]

To a solution of 4-benzyloxy-α-bromoacetophenone (467.1 mg, 1.53 mmol) in acetone (15 mL) was added guaiacol (0.19 mL, 1.68 mmol) and K₂CO₃ (213.4 mg, 1.54 mmol). This reaction mixture was heated to reflux for 4.5 h. Then it was allowed to cool to room temperature, filtered and concentrated in vacuo. The resulting solid was purified by column chromatography on silica gel (eluent: cyclohexane/EtOAc = 2/1 ~ 1/2, v/v) to afford a white yellow solid (372.9 mg, yield 70%).

\[ \text{H NMR (400 MHz, CDCl}_3\text{)} \delta 8.06 - 7.99 \ (m, 2H), 7.46 - 7.33 \ (m, 5H), 7.06 - 7.01 \ (m, 2H), 6.99 - 6.89 \ (m, 2H), 6.88 - 6.82 \ (m, 2H), 5.28 \ (s, 2H), 5.14 \ (s, 2H), 3.88 \ (s, 3H). \]

\[ \text{C NMR (126 MHz, CDCl}_3\text{)} \delta 193.15, 163.10, 149.77, 147.64, 136.06, 130.55, 128.73, 128.31, 127.94, 127.48, 122.35, 120.81, 114.81, 114.74, 112.19, 72.03, 70.20, 55.94. \]
3-hydroxy-1-(4-(benzyloxy)phenyl)-2-(2-methoxyphenoxy)propan-1-one;[16]

![Chemical Structure]

1-(4-(benzyloxy)phenyl)-2-(2-methoxyphenoxy)ethan-1-one (251.7 mg, 0.72 mmol) and K$_2$CO$_3$ (111.4 mg, 0.81 mmol) were dissolved in EtOH/acetone (v/v = 1/1, 20 mL). Then formalin solution (37 wt.%, 212.2 mg, 2.61 mmol) was added to the mixture at room temperature. The resulting mixture was stirred at r.t. for 2 h and then filtered, washed with acetone and the filtrate was concentrated in vacuo to give the crude product as an orange-pink oil. The crude product was purified by column chromatography on silica gel (elucent: petroleum ether/ethyl acetate = 4/1 ~ 1/1, v/v) to yield the product as pale-yellow oil (204.1 mg, yield: 75%).

$^1$H NMR (500 MHz, CDCl$_3$) δ 8.07 (dd, $J = 8.8, 1.6$ Hz, 2H), 7.48 – 7.29 (m, 5H), 7.05 – 6.95 (m, 3H), 6.94 – 6.86 (m, 2H), 6.85 – 6.78 (m, 1H), 5.37 (t, $J = 5.3$ Hz, 1H), 5.13 (s, 2H), 4.08 – 3.99 (m, 2H), 3.86 (s, 3H), 3.05 (t, $J = 6.6$ Hz, 1H).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ 194.99, 163.19, 150.60, 146.99, 136.01, 131.32, 128.74, 128.32, 128.16, 127.49, 123.73, 121.18, 118.83, 114.81, 112.33, 84.86, 70.21, 65.86, 63.59, 55.82, 15.28.

Lignin model substrate 8; 3-hydroxy-1-(4-hydroxyphenyl)-2-(2-methoxyphenoxy)propan-1-one;[15]

![Chemical Structure]

3-hydroxy-1-(4-(benzyloxy)phenyl)-2-(2-methoxyphenoxy)propan-1-one (154.7 mg, 0.41 mmol) and n-Bu$_4$NI (227.4 mg, 0.62 mmol) were stirred in degassed dry DCM (10 mL) in at −78°C under argon. To this, a solution of BCl$_3$ (0.62 mL, 1 M solution in hexane, 0.62 mmol) was added dropwise. The mixture was stirred at −78°C for 5 minutes upon which the reaction was allowed to warm to 0°C and was stirred for 1 h. The reaction solution was quenched with ice and H$_2$O, stirred for 30 min, diluted with saturated aqueous NaHCO$_3$ solution, and extracted with DCM. The combined organic layer was dried over Na$_2$SO$_4$ and then by filtration, concentrated, and purified by chromatography on silica gel (elucent: petroleum ether/EtOAc = 3/1 ~ 1/2, v/v) to afford the final product (108.9 mg, yield 92%) as a dark yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (dd, $J = 8.6, 6.5$ Hz, 2H), 7.04 – 6.97 (m, 1H), 6.87 (m, 5H), 5.37 (dd, $J = 8.9, 5.1$ Hz, 1H), 4.06 (d, $J = 5.2$ Hz, 2H), 3.86 (s, 3H), 3.31 – 3.23 (m, 2H).
3. Electrochemical data

Figure S2. Cyclic voltammograms of the PDI(H)-PEG (a) and PDI(Br)-PEG compounds (b) in de-aerated DMF (black traces) and in water with 0.1 M phosphate buffer (PBS) at pH 7 (red traces) at 20 °C. The supporting electrolyte in DMF was 0.1 M TBAPF₆, and in water the PBS buffer served as electrolyte. The potential scan rate was 100 mV/s in all cases. Measurements in DMF occurred in presence of a small quantity of ferrocene (Fc) as an internal reference.
Figure S3. Cyclic voltammograms of the PDI(H)-dipp (a) and PDI(Br)-dipp compounds (b) in de-aerated DMF at 20 °C. The supporting electrolyte in DMF was 0.1 M TBAPF₆, the potential scan rate was 100 mV/s in all cases. Measurements occurred in presence of a small quantity of ferrocene (Fc) as an internal reference.
In the following, we attempt to estimate the redox potential of the photoactive (luminescent) excited state of the PDI(H)-PEG\(^2\) species, because this excited-state redox potential (designated further below as \(E(\text{PDI(H)}-\text{PEG}^*/\text{PDI(H)}-\text{PEG}^2)\)) is relevant for the photocatalysis experiments, in which the excited dianion species acts as a donor of single electrons. The one-electron oxidation potential of the excited dianion was estimated with equation S1, which is commonly employed to estimate excited-state oxidation potentials (\(E_{\text{ox}}^*\)) from ground-state oxidation potentials (\(E_{\text{ox}}\) and excited-state energies (\(E_{0,0}\)); \(e\) is the elemental charge.

\[ E_{\text{ox}}^* = E_{\text{ox}} - E_{0,0} / e \]  

(eq. S1)

In our specific case, \(E_{\text{ox}}^* = E(\text{PDI(H)}-\text{PEG}^*/\text{PDI(H)}-\text{PEG}^2)\), \(E_{\text{ox}} = E(\text{PDI(H)}-\text{PEG}^*/\text{PDI(H)}-\text{PEG}^2)\), and \(E_{0,0}\) is the energy of the emissive excited state of the PDI(H)-PEG\(^2\) species. For DMF as solvent, this analysis is straightforward, and \(E_{\text{ox}}\) is readily obtained from the cyclic voltammetry data (summarized in Table 1) whereas \(E_{0,0}\) is accessible from the luminescence spectrum in Figure S10a (the emission band maximum (\(\lambda_{\text{max,em}}\)) is used as a proxy for \(E_{0,0}\)). This simple analysis yields \(E_{\text{ox}}^* = -2.73 \text{ V vs SCE}\) in DMF (upper line of Table S1).

In the cyclic voltammograms recorded in aqueous solution, the PDI/PDI\(^{-}\) and the PDI\(^{+}\)/PDI\(^2\) redox events are unresolved and are merely detectable as a two-electron redox wave. To obtain an estimate of the potential for one-electron oxidation of photoexcited PDI\(^2\) in this solvent, we approximate the half-wave potential of the PDI/PDI\(^2\) two-electron reduction as the PDI\(^{+}\)/PDI\(^2\) potential. In other words, we assume that the potential of the PDI/PDI\(^2\) two-electron wave is largely governed by the secondary reduction process from PDI\(^{+}\) to PDI\(^2\) (rather than the primary reduction event leading from PDI to PDI\(^{+}\)). This is a crude approximation, but at least it allows a rough estimate of the one-electron oxidation potential of the photoexcited PDI(H)-PEG\(^2\) species in aqueous solution (lower line of Table S1).

**Table S1.** Estimation of the electrochemical potential for one-electron oxidation of the photoexcited PDI(H)-PEG\(^2\) species in different solvents. See text above for definitions of parameters and further details.

| solvent | \(E(\text{PDI(H)}-\text{PEG}^*/\text{PDI(H)}-\text{PEG}^2)\) / V vs SCE | \(\lambda_{\text{max,em}}\) / nm | \(E_{0,0}\) / eV | \(E(\text{PDI(H)}-\text{PEG}^*/\text{PDI(H)}-\text{PEG}^2)\) / V vs SCE |
|---------|-----------------------------|------------------|---------------|-----------------------------|
| DMF     | -0.80                       | 644              | 1.93          | -2.73                       |
| H\(_2\)O | -0.65                       | 623              | 1.99          | -2.65                       |
To determine the reduction potentials of substrates 1 – 3 and 4-chlorobenzoate in DMF, ammonium salts of these compounds were formed using TBAOH solution in methanol under argon.\textsuperscript{[18]} Cyclic voltammograms of the ammonium benzoate salts in 0.1 M tetra-\textit{n}-butylammonium hexafluorophosphate (TBAPF\textsubscript{6}) were then measured in dry and deaerated DMF in a glovebox. A glassy carbon electrode was employed as working electrode, and silver wires were used as counter and reference electrodes. The potential scan rate was 100 mV/s, and ferrocene was used as an internal reference in all four measurements.

\textbf{Figure S4.} Cyclic voltammograms of substrates 1, 2, 3, and 4-chlorobenzoate (from top to bottom) in deaerated DMF at 20 °C. Measurements occurred in presence of a small quantity of ferrocene (Fc) as an internal reference. The blue line in the bottom voltammogram was obtained from a solution without 4-chlorobenzoate (blank).
Table S2. Reduction potentials determined from the cyclic voltammetry data in Figure S4.

| compound                  | $E$ (V vs SCE) |
|---------------------------|----------------|
| substrate 1               | -2.5           |
| substrate 2               | -2.5           |
| substrate 3               | -2.8           |
| 4-chlorobenzoate          | -2.9           |

It seems noteworthy that 4-(trifluoromethyl)benzoate (substrate 3) exhibits a reduction potential that is roughly 0.3 V more negative than that of 4-(trifluoromethyl)benzene, for which a prior study reported a value of -2.5 V vs SCE in DMF.\textsuperscript{[19]}
4. Additional optical spectroscopic data

**Figure S5.** UV-Vis absorption spectra of the PDI(H)-PEG compound in three different oxidation states including the charge-neutral (PDI, blue), monoanion (PDI\(^{-}\), green) and dianion form (PDI\(^{2-}\), black) in de-aerated DMF (a) and water (b) at 20 °C. Optical densities were normalized to 1.0 at the respective absorption maxima in the visible range for better visualization and comparison. Extinction coefficients (ε) at selected wavelengths are given in Table S3.
Figure S6. UV-Vis absorption spectra of the PDI(Br)-PEG compound in three different oxidation states including the charge-neutral (PDI, blue), monoanion (PDI\(^{\cdot -}\), green) and dianion form (PDI\(^{2-}\), black) in de-aerated DMF (a) and water (b) at 20 °C. Optical densities were normalized to 1.0 at the respective absorption maxima in the visible range for better visualization. Extinction coefficients (\(\varepsilon\)) at selected wavelengths are given in Table S3. The asterisk (*) marks an artefact caused by a detector change.
For the lipophilic PDI(H/Br)-dipp compounds, a comparison of UV-Vis spectra in DMF and water is not possible due to insufficient solubility in water. For these compounds, merely the UV-Vis spectra of neutral, monoanion and dianion forms in DMF were measurable (Figure S7).

**Figure S7.** UV-Vis absorption spectra of the PDI(Br)-dipp compound in three different oxidation states including the charge-neutral (PDI, blue), monoanion (PDI\(^{-}\), green) and dianion form (PDI\(^{2-}\), black) in de-aerated DMF (a) and water (b) at 20 °C. Optical densities were normalized to 1.0 at the respective absorption maxima in the visible range for better visualization. Extinction coefficients (ε) at selected wavelengths are given in Table S3. The asterisk (*) marks an artefact caused by a detector change.
The individual UV-Vis absorption spectra in Figures S5/S6/S7 were normalized to optical densities of 1.0 at the respective absorption band maxima ($\lambda_{\text{abs,max}}$) in the visible spectral range for better visualization and comparison. Table S3 summarizes the extinction coefficients ($\varepsilon$) at the respective absorption band maxima. Furthermore, it includes the emission band maxima ($\lambda_{\text{em,max}}$) for all neutral and dianion species; the monoanion forms are not luminescent.

**Table S3.** Absorption ($\lambda_{\text{abs,max}}$) and emission band maxima ($\lambda_{\text{em,max}}$), along with extinction coefficients ($\varepsilon$) of the different compounds in DMF and H$_2$O.

| compound          | solvent | $\lambda_{\text{abs,max}}$ / nm | $\varepsilon$ / M$^{-1}$ cm$^{-1}$ | $\lambda_{\text{em,max}}$ / nm |
|-------------------|---------|---------------------------------|-----------------------------------|-------------------------------|
| PDI(H)-dipp$^{2-}$ | DMF     | 568                            | 9.44·10$^4$                       | 664                           |
| PDI(H)-dipp       | DMF     | 527                            | 7.05·10$^4$                       | 547                           |
| PDI(Br)-dipp$^{2-}$ | DMF   | 635                            | 3.86·10$^4$                       | 731                           |
| PDI(Br)-dipp      | DMF     | 528                            | 4.12·10$^4$                       | 559                           |
| PDI(H)-PEG$^{2-}$ | DMF     | 565                            | 3.23·10$^4$                       | 644                           |
| PDI(H)-PEG        | DMF     | 525                            | 2.38·10$^4$                       | 538                           |
| PDI(Br)-PEG$^{2-}$ | DMF   | 628                            | 6.00·10$^4$                       | 709                           |
| PDI(Br)-PEG       | DMF     | 524                            | 5.04·10$^4$                       | 555                           |
| PDI(H)-PEG$^{2-}$ | H$_2$O  | 540                            | 5.70·10$^4$                       | 623                           |
| PDI(H)-PEG        | H$_2$O  | 496                            | 1.98·10$^4$                       | 545                           |
| PDI(Br)-PEG$^{2-}$ | H$_2$O | 540                            | 9.14·10$^3$                       | 628                           |
| PDI(Br)-PEG       | H$_2$O  | 497                            | 3.91·10$^3$                       | 561                           |
Figure S8. UV-Vis absorption (black traces) and photoluminescence spectra (red traces) of the dianion forms of the PDI(H)-PEG (a) and PDI(Br)-PEG compounds (c) in water under Argon at 20 °C. Luminescence decays of PDI(H)-PEG$^2^-$ (b) and PDI(Br)-PEG$^2^-$ (d) detected at 623 and 628 nm under the same conditions. Excitation occurred at 475 and 545 nm for the steady-state measurements (a, c), respectively; and at 473 nm for the time-correlated single photon counting (TCSPC) experiments. Na$_2$S$_2$O$_4$ was present in approximately 1000-fold excess relative to the PDI chromophore in this experiment.
Figure S9. UV-Vis absorption (black traces) and photoluminescence spectra (red traces) of the charge-neutral forms of the PDI(H)-PEG (a) and PDI(Br)-PEG compounds (c) in water under Argon at 20 °C. Luminescence decays of PDI(H)-PEG (b) and PDI(Br)-PEG (d) detected at 538 and 560 nm under the same conditions. Excitation occurred at 475 nm for the steady-state measurements (a, c) and at 473 nm for the time-correlated single photon counting (TCSPC) experiment.
Figure S10. UV-Vis absorption (black traces) and photoluminescence spectra (red traces) of the dianion forms of the PDI(H)-PEG (a) and PDI(Br)-PEG compounds (c) in DMF under Argon at 20 °C. Luminescence decays of PDI(H)-PEG\textsuperscript{2-} (b) and PDI(Br)-PEG\textsuperscript{2-} (d) detected at 644 and 715 nm under the same conditions. Excitation occurred at 525 and 600 nm for the steady-state measurements (a, c), respectively; and at 473 nm for the time-correlated single photon counting (TCSPC) experiment. Approximately 5 equivalents of organic super electron donor were used to generate the PDI dianion form in this experiment.
Figure S11. UV-Vis absorption (black traces) and photoluminescence spectra (red traces) of the charge-neutral forms of the PDI(H)-PEG (a) and PDI(Br)-PEG compounds (c) in DMF under Argon at 20 °C. Luminescence decays of PDI(H)-PEG (b) and PDI(Br)-PEG (d) detected at 540 and 560 nm under the same conditions. Excitation occurred at 475 nm for the steady-state measurements (a, c) and at 473 nm for the time-correlated single photon counting (TCSPC) experiment.
**Figure S12.** UV-Vis absorption (black traces) and photoluminescence spectra (red traces) of the dianion forms of the PDI(H)-dipp (a) and PDI(Br)-dipp compounds (c) in DMF under Argon at 20 °C. Luminescence decays of PDI(H)-PEG$^{2-}$ (b) and PDI(Br)-dipp$^{2-}$ (d) detected at 665 and 720 nm under the same conditions. Excitation occurred at 475 and 635 nm for the steady-state measurements (a, c), respectively; and at 473 nm for the time-correlated single photon counting (TCSPC) experiment. Approximately 5 equivalents of organic super electron donor were used to generate the PDI dianion form in this experiment.
Figure S13. UV-Vis absorption (black traces) and photoluminescence spectra (red traces) of the charge-neutral forms of the PDI(H)-dipp (a) and PDI(Br)-dipp compounds (c) in DMF under Argon at 20 °C. Luminescence decays of PDI(H)-PEG (b) and PDI(Br)-dipp (d) detected at 580 and 560 nm under the same conditions. Excitation occurred at 490 nm for the steady-state measurements (a, c) and at 473 nm for the time-correlated single photon counting (TCSPC) experiment.
Table S4. Natural excited-state lifetimes ($\tau_0$) of the charge-neutral PDI forms in DMF and H$_2$O under Argon at 20 °C.

| compound       | DMF $\tau_0$ / ns | H$_2$O $\tau_0$ / ns |
|----------------|-------------------|-----------------------|
| PDI(H)-dipp    | 4.9               | -                     |
| PDI(Br)-dipp   | 4.9               | -                     |
| PDI(H)-PEG     | 4.7               | 4.6                   |
| PDI(Br)-PEG    | 5.3               | 5.2                   |
Figure S14. Transient absorption experiments with 50 μM PDI(H)-PEG\(^2\) in 50 mM aqueous NaOH, formed in situ in the presence of excess Na\(_2\)S\(_2\)O\(_4\) (approximately 1000 equivalents in this experiment). (a) Solid red trace: spectrum obtained by time-integration over an interval of 5 μs immediately after excitation at 532 nm with laser pulses of ca. 10 ns duration. Dashed blue trace: Difference spectrum resulting from the subtraction of the absorption spectrum of PDI(H)-PEG\(^2\) from the absorption spectrum of PDI(H)-PEG\(^+\); the respective absorption spectra (measured in aqueous solution) were scaled to an identical optical density at 578 nm prior to the subtraction. (b) Transient absorption spectra of the same solution as in (a), recorded with different delay times as indicated in the inset. The temporal evolution of the transient absorption signal at 640 nm and the bleach at 532 nm is shown on 100 μs (c, d) and 800 μs timescales (d, f).
Figure S15. Photostability of 40 μM PDI(H)-PEG in de-aerated 50 mM aqueous NaOH solution in presence of excess Na₂S₂O₄ at 20 °C. (a) Absorption spectra were measured after different time intervals following irradiation at 505 nm with an LED (200 mW). The individual spectra were offset by 0.2 relative to each other for better visualization. (b) Absorbance of the respective solution at selected wavelengths as marked by the dotted arrows (505, 540, 605 nm).
Figure S16. Stern-Volmer luminescence quenching experiments with PDI(H)-PEG\textsuperscript{2−} and 4-bromo-2-chloro-3-fluorobenzoate (substrate 1) in aqueous solution containing 50 mM NaOH at 20 °C. Excitation of PDI(H)-PEG\textsuperscript{2−} occurred at 473 nm, and the luminescence decays (a) were monitored at 623 nm in presence of excess Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} (approximately 1000 equivalents with respect to the PDI chromophore) under Argon. The concentrations of 4-bromo-2-chloro-3-fluorobenzoate were as indicated in the inset. (b) Stern-Volmer plot resulting from the data luminescence lifetime in (a); the dotted black line is the result of a linear regression fit, yielding a Stern-Volmer constant (K\textsubscript{SV}) of 9.77 M\textsuperscript{−1}.

Figure S17. Stern-Volmer luminescence quenching experiments with PDI(H)-PEG\textsuperscript{2−} and 4-bromo-3-(trifluoromethyl)benzoate (substrate 2) in aqueous solution containing 50 mM NaOH at 20 °C. Excitation of PDI(H)-PEG\textsuperscript{2−} occurred at 473 nm, and the luminescence decays (a) were monitored at 623 nm in presence of excess Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} (approximately 1000 equivalents with respect to the PDI chromophore) under Argon. The concentrations of 4-bromo-3-(trifluoromethyl)benzoate were as indicated in the inset. (b) Stern-Volmer plot resulting from the data luminescence lifetime in (a); the dotted black line is the result of a linear regression fit, yielding a Stern-Volmer constant (K\textsubscript{SV}) of 15.23 M\textsuperscript{−1}.
Figure S18. Stern-Volmer luminescence quenching experiments with PDI(H)-PEG\textsuperscript{2} and 4-(trifluoromethyl)benzoate (substrate 3) in aqueous solution containing 50 mM NaOH at 20 °C. Excitation of PDI(H)-PEG\textsuperscript{2} occurred at 473 nm, and the luminescence decays (a) were monitored at 623 nm in presence of excess Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} (approximately 1000 equivalents with respect to the PDI chromophore) under Argon. The concentrations of 4-(trifluoromethyl)benzoate were as indicated in the inset. (b) Stern-Volmer plot resulting from the data luminescence lifetime in (a); the dotted black line is the result of a linear regression fit, yielding a Stern-Volmer constant (K\textsubscript{SV}) of 11.26 M\textsuperscript{-1}.

Figure S19. Stern-Volmer luminescence quenching experiments with PDI(H)-PEG\textsuperscript{2} and 4-chlorobenzoate in aqueous solution containing 50 mM NaOH at 20 °C. Excitation of PDI(H)-PEG\textsuperscript{2} occurred at 473 nm, and the luminescence decays (a) were monitored at 623 nm in the presence of excess Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} (approximately 1000 equivalents with respect to the PDI chromophore) under Argon. The concentrations of 4-(trifluoromethyl)benzoate were as indicated in the inset. (b) Stern-Volmer plot resulting from the data luminescence lifetime in (a); the dotted black line is the result of a linear regression fit, yielding a Stern-Volmer constant (K\textsubscript{SV}) of 7.21 M\textsuperscript{-1}.
Figure S20. Luminescence quenching experiments with PDI(H)-PEG (in its charge-neutral form) and 4-bromo-2-chloro-3-fluorobenzoate (substrate 1) in aqueous solution containing 50 mM NaOH at 20 °C. Excitation of PDI(H)-PEG occurred at 473 nm, and the luminescence decays (a) were monitored at 545 nm under Argon. The concentrations of 4-bromo-2-chloro-3-fluorobenzoate were as indicated in the inset. (b) Stern-Volmer plot resulting from the data luminescence lifetime in (a); the dotted black line is the result of a linear regression fit. This data set indicates that substrate 1 does not quench the luminescence emitted by charge-neutral PDI(H)-PEG in water.

Figure S21. Luminescence quenching experiments with PDI(H)-PEG (in its charge-neutral form) and 4-bromo-3-(trifluoromethyl)benzoate (substrate 2) in aqueous solution containing 50 mM NaOH at 20 °C. Excitation of PDI(H)-PEG occurred at 473 nm, and the luminescence decays (a) were monitored at 545 nm under Argon. The concentrations of 4-bromo-3-(trifluoromethyl)benzoate were as indicated in the inset. (b) Stern-Volmer plot resulting from the data luminescence lifetime in (a); the dotted black line is the result of a linear regression fit. This data set indicates that substrate 2 does not quench the luminescence emitted by charge-neutral PDI(H)-PEG in water.
Figure S22. Luminescence quenching experiments with PDI(H)-PEG (in its charge-neutral form) and 4-(trifluoromethyl)benzoate (substrate 3) in aqueous solution containing 50 mM NaOH at 20 °C. Excitation of PDI(H)-PEG occurred at 473 nm, and the luminescence decays (a) were monitored at 545 nm under Argon. The concentrations of 4-(trifluoromethyl)benzoate were as indicated in the inset. (b) Stern-Volmer plot resulting from the data luminescence lifetime in (a); the dotted black line is the result of a linear regression fit. This data set indicates that substrate 3 does not quench the luminescence emitted by charge-neutral PDI(H)-PEG in water.

Figure S23. Luminescence quenching experiments with PDI(H)-PEG (in its charge-neutral form) and 4-chlorobenzoate in aqueous solution containing 50 mM NaOH at 20 °C. Excitation of PDI(H)-PEG occurred at 473 nm, and the luminescence decays (a) were monitored at 545 nm under Argon. The concentrations of 4-(trifluoromethyl)benzoate were as indicated in the inset. (b) Stern-Volmer plot resulting from the data luminescence lifetime in (a); the dotted black line is the result of a linear regression fit. This data set indicates that substrate 4 does not quench the luminescence emitted by charge-neutral PDI(H)-PEG in water.
Table S5. Rate constants for excited-state deactivation of the dianion and the neutral forms of PDI(H)-PEG by various substrates in aqueous solution at room temperature.

| substrate | PDI$^{2-}$  | PDI$^0$  |
|-----------|-------------|----------|
|           | $k_0$ / M$^{-1}$ s$^{-1}$ | $k_0$ / M$^{-1}$ s$^{-1}$ |
| 1         | $1.55 \cdot 10^9$ | $< 10^9$ |
| 2         | $2.42 \cdot 10^9$ | $< 10^9$ |
| 3         | $1.79 \cdot 10^9$ | $< 10^9$ |
| 4         | $1.15 \cdot 10^9$ | $< 10^9$ |

$^a$ Measured in ultrapure water containing 50 mM NaOH in the presence of excess Na$_2$S$_2$O$_4$ under Argon. $^b$ Measured in ultrapure water containing 50 mM NaOH under Argon.
5. Photochemical reactions

Photoreactions in aqueous solution were performed in Millipore MilliQ water. Reaction progress was followed by $^{19}$F NMR spectroscopy using trifluoroacetic acid (TFA) as internal standard. (376 MHz, alkaline H$_2$O containing 10 % D$_2$O for shimming and locking). Quantitative $^{19}$F NMR experiments (to determine substrate turnovers and product yields) were carried out with proton decoupling.

Table S6. $^{19}$F-NMR spectral data of some compounds relevant to the photoreaction of substrate 3 in alkaline aqueous solution.\cite{footnote1}

| compound | short name | $\delta$ / ppm |
|----------|------------|----------------|
| ![F3C] | 3 | -63.2 (s) |
| ![HF2C] | | -111.5 (d, $^2J_{H,F} = 56$ Hz) |
| ![DF2C] | | -112.2 (1:1:1, t, $^2J_{D,F} = 9$ Hz) |
| ![H2FC] | | -206.2 (t, $^2J_{H,F} = 48$ Hz) |
| ![3-P] | 3-P | -112.9 (s) |
| ![F] | | -120.4 |

**General procedure (A) for C–Br bond activation in water:** The aryl halogenide substrate (0.019 mmol), trifluoroacetic acid (1.40 μL, 2.1 mg, 0.019 mmol), isopropanol (400 μL, 5.22 mmol) and PDI(H)-PEG (0.001 mmol) were dissolved in 1.5 mL 50 mM aqueous NaOH solution. The mixture was degassed in three freeze-pump-thaw cycles. Then this mixture was added to a 5 mL vial containing Na$_2$S$_2$O$_4$ (0.1 mmol) under Ar. The reaction mixture was irradiated at 525 nm (LED, the maximum output power was 40 W) under Ar at room temperature in a water bath. After 24 h, an additional portion of degassed solution of PDI(H)-PEG (0.001 mmol) mixed with Na$_2$S$_2$O$_4$ (0.1 mmol) was added to the reaction mixture under Ar, and the photoreaction was continued for another 24 h. The crude product was obtained after acidification of the aqueous reaction mixture with concentrated H$_2$SO$_4$ and subsequent extraction with diethyl ether and ethyl acetate.

**Procedure (B) for C–F bond activation in water:** 4-(trifluoromethyl) benzoic acid (0.019 mmol), trifluoroacetic acid (1.40 μL, 2.1 mg, 0.019 mmol) and PDI(H)-PEG (0.002 mmol) dissolved in 1.9 mL 50 mM aqueous NaOH solution. The mixture was degassed in three freeze-pump-thaw cycles. Then this mixture was added to a 5 mL vial containing
Na$_2$S$_2$O$_4$ (0.40 mmol) under Ar. The reaction mixture was irradiated at 525 or 390 nm (LED, the maximum output power was 40 W) under Ar for 24 h at room temperature in a water bath. The crude product was obtained after acidification of the aqueous reaction mixture with concentrated H$_2$SO$_4$ and subsequent extraction with diethyl ether and ethyl acetate.

**Procedure (C) for the photodegradation of chloroacetate in water:** sodium chloroacetate (0.02 mmol), sodium 3-(trimethylsilyl)propane-1-sulfonate (DSS, 4.4 mg, 0.02 mmol, used here as NMR standard) and PDI(H)-PEG (0.002 mmol) were dissolved in 2.0 mL 50 mM aqueous NaOH solution. The mixture was degassed with three freeze-pump-thaw cycles, and then this mixture was added to a 5 mL vial containing Na$_2$S$_2$O$_4$ (0.40 mmol) under Ar. The reaction mixture (and the reference sample containing no Na$_2$S$_2$O$_4$) were irradiated at 525 nm (LED, the maximum output power was 40 W) under Ar for 17 h at room temperature in a water bath. For $^1$H NMR spectroscopy, 10% D$_2$O was added to the reaction mixture and the reference sample.

**General procedure (D) for reductive C–O bond cleavage in the biphasic MeCN-H$_2$O system:** The substrate (0.25 mmol, 1.00 equiv) and PDI(H)-dipp (0.0027 mmol, 1 mol%) were dissolved in 1.5 mL MeCN (Sigma, >98%, sealed bottle). The mixture was degassed in three freeze-pump-thaw cycles. Then this mixture was added to a 5 mL vial containing 2 mL ultrapure aqueous solution of Na$_2$S$_2$O$_4$ (0.75 mmol, 3 equivalents) and TBACl (0.05 mmol, 0.2 equivalents) under Ar. The reaction mixture was irradiated at 525 nm with an LED (maximum output power of 40 W) under Ar at room temperature (while cooling with a water bath) for 24 h. After adding 2 mL of deionized water, the organic and aqueous layers were separated from each other, and the aqueous phase was extracted with EtOAc (2 × 10 mL). The combined organic phases were dried over anhydrous Na$_2$S$_2$O$_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired products.

Under photocatalysis conditions (procedure A – D), the molar ratio between Na$_2$S$_2$O$_4$ and PDI is 100:1 or greater. The UV-Vis absorption spectrum in Figure S24 was recorded under such conditions, and it confirms that PDI$^{2-}$ is by far the dominant visible-light absorbing species under these conditions. The spectrum in Figure S24 is essentially identical to that of PDI(H)-PEG$^{2-}$ in Figures 2d / S5b.

![Figure S24](image.png)

**Figure S24.** UV-Vis absorption spectrum of PDI(H)-PEG in the presence of 100 equivalents of Na$_2$S$_2$O$_4$ in deaerated water containing 50 mM NaOH at room temperature. PDI dianion is formed in essentially quantitative fashion.
NMR spectra for the photoreaction of substrate 1 (4-bromo-2-chloro-3-fluorobenzoate):

Figure S25. $^{19}$F NMR spectra resulting from a control experiment performed with the 4-bromo-2-chloro-5-fluorobenzoate substrate and trifluoroacetate (TFA) as internal standard. The reaction mixture contained 400 μL isopropanol and 1 mM PDI(H)-PEG, but no Na$_2$S$_2$O$_4$. The sample was irradiated at 525 nm. Top (green line): $^{19}$F NMR spectrum recorded before irradiation ($t = 0$ h). Bottom (red line): $^{19}$F NMR spectrum recorded after irradiation ($t = 24$ h).

In this control experiment without Na$_2$S$_2$O$_4$, no significant substrate conversion and product formation are observable, confirming that the Na$_2$S$_2$O$_4$ reductant is indispensable.
**Figure S26.** $^{19}$F NMR spectra resulting from a control experiment performed with the 4-bromo-2-chloro-5-fluorobenzoate substrate and trifluoroacetate (TFA) as internal standard. The reaction mixture contained 400 μL isopropanol and excess Na$_2$S$_2$O$_4$ (0.4 mmol), but no PDI(H)-PEG. The sample was irradiated at 525 nm. Top (green line): $^{19}$F NMR spectrum recorded before irradiation (t = 0 h). Bottom (red line): $^{19}$F NMR spectrum recorded after irradiation (t = 24 h).

In this control experiment without PDI(H)-PEG, no significant substrate conversion and product formation are observable, confirming that the PDI(H)-PEG photosensitizer is indispensable.
Figure S27. $^{19}$F NMR spectra resulting from the main experiment performed with the 4-bromo-2-chloro-5-fluorobenzoate substrate (1) and trifluoroacetate (TFA) as internal standard. The reaction mixture contained 400 μL isopropanol, 1 mM PDI(H)-PEG and excess Na$_2$S$_2$O$_4$ (total amount of 0.2 mmol). The sample was irradiated at 525 nm (the maximum output power was 40 W). Top spectrum (purple trace): $^{19}$F spectrum before the irradiation ($t = 0$ h). Middle spectrum (green trace): $^{19}$F spectrum after the irradiation ($t = 48$ h). Bottom spectrum (red trace): $^{19}$F spectrum of the reference debromination product, 2-chloro-5-fluorobenzoate (commercially available).

The conversion of the starting material was 69%, and the yield of the debromination product was 60%.
Figure S28. $^1$H NMR spectrum (in CD$_3$CN) of the crude sample after workup of the green light-driven reductive debromination reaction with 4-bromo-2-chloro-5-fluorobenzoate (substrate 1). The crude product was obtained after acidification of the aqueous reaction mixture with H$_2$SO$_4$ and subsequent extraction with diethyl ether and ethyl acetate, as described above.

The $^1$H NMR spectrum after 48 h of irradiation is in good agreement with the reference spectrum of the commercially available debromination product.
Figure S29. $^{19}$F NMR spectrum of the same sample as in Figure S28.
NMR spectra for the photoreaction of substrate 2 (4-bromo-3-(trifluoromethyl)benzoate):

**Figure S30.** $^{19}$F NMR spectra resulting from a control experiment performed with the 4-bromo-3-trifluoromethyl benzoate substrate (2) and trifluoroacetate (TFA) as internal standard. The reaction mixture contained 400 μL isopropanol and 1 mM PDI(H)-PEG, but no Na$_2$S$_2$O$_4$. The sample was irradiated at 525 nm. Top (green trace): $^{19}$F NMR spectrum recorded before irradiation ($t = 0$ h). Bottom (red trace): $^{19}$F NMR spectrum recorded after irradiation ($t = 24$ h).

In this control experiments without Na$_2$S$_2$O$_4$, no significant substrate conversion and product formation are observable, confirming that the Na$_2$S$_2$O$_4$ reductant is indispensable.
**Figure S31.** $^{19}$F NMR spectra resulting from a control experiment performed with the 4-bromo-3-trifluoromethyl benzoate substrate (2) and trifluoroacetate (TFA) as internal standard. The reaction mixture contained 400 μL isopropanol and excess Na$_2$S$_2$O$_4$ (0.4 mmol), but no PDI(H)-PEG. The sample was irradiated at 525 nm. Top (green trace): $^{19}$F NMR spectrum recorded before irradiation ($t = 0$ h). Bottom (red trace): $^{19}$F NMR spectrum recorded after irradiation ($t = 24$ h).

In this control experiment without PDI(H)-PEG, no significant substrate conversion and product formation are observable, confirming that the PDI(H)-PEG photosensitizer is indispensable.
Figure S32. $^{19}$F NMR spectra resulting from the main experiment performed with the 4-bromo-3-trifluoromethyl benzoate substrate (2) and trifluoroacetate (TFA) as internal standard. The reaction mixture contained 400 μL isopropanol, 1 mM PDI(H)-PEG and excess Na₂S₂O₄ (total amount of 0.2 mmol). The sample was irradiated at 525 nm (the maximum output power was 40 W). Top spectrum (dark blue trace): $^{19}$F spectrum before the irradiation ($t = 0$ h). Middle spectrum (green trace): $^{19}$F spectrum after 48 h of irradiation. Bottom spectrum (red trace): $^{19}$F spectrum of the reference debromination product, 3-trifluoromethyl benzoate (commercially available).

The conversion of the starting material was almost 96%, and the yield of the debromination product was 60% according to the $^{19}$F spectrum.
Figure S33. Top (dark blue trace): $^1$H NMR spectrum (in CD$_3$CN) of the crude product after workup of the green light driven reductive debromination of 4-bromo-3-trifluoromethyl benzoate (2). The crude product was obtained after acidification of the aqueous reaction mixture with H$_2$SO$_4$ and subsequent extraction with diethyl ether and ethyl acetate, as described above. Middle (green trace): $^1$H NMR spectrum (in CD$_3$CN) of the starting material. Bottom (red trace): $^1$H NMR spectrum (in CD$_3$CN) of the reference compound, 3-trifluoromethyl benzoic acid (commercially available).
The results in Figure S33 and Figure S34 show that the conversion of the 4-bromo-3-(trifluoromethyl)benzoate (2) is almost complete. The main signal of the debromination product in the $^{19}$F NMR spectrum is at −63.38 ppm, and the $^1$H NMR spectrum after 48 h of irradiation is in excellent agreement with the reference spectrum of the commercially available debromination product.
NMR spectra for the photoreaction of substrate 3 (4-(trifluoromethyl)benzoate):

Figure S35. $^{19}$F NMR spectrum resulting from a control experiment performed with 4-(trifluoromethyl)benzoate substrate (3) and trifluoroacetate (TFA) as internal standard. The reaction mixture contained 1 mM PDI(H)-PEG, but no Na$_2$S$_2$O$_4$. The sample was irradiated at 390 nm (the maximum output power was 40 W). Top (green trace): $^{19}$F NMR spectra recorded before irradiation ($t = 0$ h). Bottom (red trace): $^{19}$F NMR spectrum recorded after irradiation ($t = 24$ h).

In this control experiment without Na$_2$S$_2$O$_4$, no significant substrate conversion and product formation are observable, confirming that the Na$_2$S$_2$O$_4$ reductant is indispensable.
Figure S36. $^{19}$F NMR spectra resulting from a control experiment performed with the 4-(trifluoromethyl)benzoate substrate (3) and trifluoroacetate (TFA) as internal standard. The reaction mixture contained excess Na$_2$S$_2$O$_4$ (0.40 mmol), but no PDI(H)-PEG. The sample was irradiated at 390 nm (the maximum output power was 40 W). Top (green trace): $^{19}$F NMR spectrum recorded before irradiation ($t = 0$ h). Bottom (red trace): $^{19}$F NMR spectrum recorded after irradiation ($t = 24$ h).

In this control experiments without PDI(H)-PEG, no significant substrate conversion and product formation are observable, confirming that the PDI(H)-PEG photosensitizer is indispensable.
Figure S37. $^{19}$F NMR spectrum resulting from the experiment performed with the 4-(trifluoromethyl)benzoate substrate (3) and trifluoroacetate (TFA) as internal standard. The reaction mixture contained excess Na$_2$S$_2$O$_4$ (0.40 mmol) and 1 mM PDI(H)-PEG. The sample was irradiated at 390 nm (the maximum output power was 40 W). Top (green trace): $^{19}$F NMR spectrum recorded before irradiation ($t = 0$ h). Bottom (red trace): $^{19}$F NMR spectra recorded after irradiation ($t = 24$ h).

The $^{19}$F NMR spectrum recorded after 24 h of irradiation features a resonance at −112.58 ppm (s), which is attributable to the dimer shown in Figure S37 (−112.9 ppm (s) according to Table S6). The conversion of the starting material is 84%. The yield of the dimer is 36%.
Figure S38. Top (green trace): $^1$H NMR spectrum (in CD$_3$CN) of the crude product after workup of the photoreaction of the 4-(trifluoromethyl)benzoate substrate (3) following irradiation at 390 nm for 24 h. Bottom (red trace): $^1$H NMR spectrum (in CD$_3$CN) of the starting material. The crude product was obtained after acidification of the aqueous reaction mixture with H$_2$S$_2$O$_4$ and subsequent extraction with diethyl ether and ethyl acetate, as described above.

The complete reaction system containing PDI(H)-PEG and Na$_2$S$_2$O$_4$, showed significant substrate conversion and dimer product formation. The resonance signal of the radical dimerization product, 4,4'-((tetrafluoroethane-1,2-diyl)dibenzoate, formed after the mono-defluorination, is observable at −112.58 ppm (Figure S37, Table S6), and the $^1$H NMR spectrum in Figure S38 shows two new resonances at 8.12 and 7.63 ppm, which are attributable to the dimer product.
NMR spectra for the photodegradation of chloroacetate:

Figure S39. $^1$H NMR spectra resulting from the chloroacetate photodegradation experiment according to procedure C (main sample with excitation and control sample in the dark), using sodium 3-(trimethylsilyl)propane-1-sulfonate (DSS) as internal standard. The solvent was 90% H$_2$O and 10% D$_2$O. Top (dark blue trace): $^1$H NMR spectrum prior to irradiation. Middle (green trace): $^1$H NMR spectrum after 17 h of irradiation at 525 nm. Bottom (red trace): $^1$H NMR spectrum after 17 h in the dark.

The conversion of the starting material amounts to 65% based on the reference signal of the internal DSS standard under light irradiation, whilst in the dark 18% of the initially present chloroacetate decompose over the same time span.
Figure S40. $^1$H NMR spectra resulting from the chloroacetate photodegradation control experiment according to procedure C (reference sample containing no Na$_2$S$_2$O$_4$), using sodium 3-(trimethylsilyl)propane-1-sulfonate (DSS) as internal standard. The solvent was 90% H$_2$O and 10% D$_2$O. Top (green trace): $^1$H NMR spectrum prior to irradiation. Bottom (red trace): $^1$H NMR spectrum after 17 h of irradiation at 525 nm.

In this control experiment without Na$_2$S$_2$O$_4$, no significant substrate conversion and formation of new products is observable, confirming that the Na$_2$S$_2$O$_4$ reductant is indispensable for the photodegradation of chloroacetate.
NMR spectra for the photoreaction of lignin model substrate 4 (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone):

Figure S41. Top (green trace): $^1$H NMR spectrum (in CDCl$_3$) of the starting material before photo-irradiation. Bottom (red trace): $^1$H NMR spectrum (in CDCl$_3$) of the control experiment sample after 24 h of photo-irradiation at 525 nm in absence of Na$_2$S$_2$O$_4$, recorded after workup and purification. The starting material (54.0 mg, recycled yield 80%) was recovered following purification by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1 ~ 2/1, v/v).

In this control experiment without Na$_2$S$_2$O$_4$, no significant substrate conversion and product formation are observable, confirming that the Na$_2$S$_2$O$_4$ reductant is indispensable.
Figure S42. Top (green trace): $^1$H NMR spectrum (in CDCl$_3$) of the starting material before photo-irradiation. Bottom (red trace): $^1$H NMR spectrum (in CDCl$_3$) of the control experiment sample after 24 h of photo-irradiation at 525 nm in absence of PDI(H)-dipp, recorded after workup and purification. The starting material (44.1 mg, recycled yield 70%) was recovered after purification by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1 ~ 2/1, v/v).

In this control experiment without PDI(H)-dipp, no significant substrate conversion and product formation are observable, confirming that the PDI(H)-dipp photocatalyst is indispensable.
Figure S43. Top (green trace): $^1$H NMR spectrum (in CDCl$_3$) of the starting material before photo-irradiation. Bottom (red trace): $^1$H NMR spectrum (in CDCl$_3$) of an experiment in which a sample containing all reaction components except TBACl was irradiated at 525 nm for 24 hours, recorded after workup and purification. The targeted C$_a$–O bond cleavage product (4-P) was clearly observable (13.4 mg, yield: 37%) after chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1 ~ 2/1, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.94 (d, $J = 8.9$ Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H).

In this control experiment without TBACl, some substrate conversion and product formation are observable, indicating that TBACl is not indispensable. However, the product yield was sub-optimal, and the starting material was partially recovered (14.5 mg, recycled yield 22%) after chromatography on silica gel (eluent: Petroleum Ether/Ethyl Acetate = 5/1 ~ 2/1).
Figure S44. Top (green trace): $^1$H NMR spectrum (in CDCl$_3$) of the starting material before photo-irradiation. Bottom (red trace): $^1$H NMR spectrum (in CDCl$_3$) of the main experiment sample (containing all reaction components) following irradiation at 525 nm for 24 hours, recorded after workup and purification. The targeted C$_\alpha$–O bond cleavage product (23.3 mg, yield 62%) was isolated and purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1 ~ 2/1, v/v).
Table S7. Summary of the photo-degradation studies with the lignin model substrate 4 (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone). Irradiation occurred with an LED at 525 nm (40 W) under Argon at room temperature for 24 hours in all cases. The solvents were H$_2$O (2 mL) and MeCN (1.5 mL) in all cases.

| Entry | PDI(H)-dipp (mmol) | Na$_2$S$_2$O$_4$ (mmol) | TBACl (mmol) | Product | Yield$^a$ |
|-------|---------------------|-------------------------|--------------|---------|-----------|
| 1     | 0.0027              | 0.75                    | 0.05         | ![Product Image] | 62%       |
| 2     | –                   | 0.75                    | 0.05         | N/A     | 0%        |
| 3     | 0.0023              | –                       | 0.05         | N/A     | 0%        |
| 4     | 0.0023              | 0.75                    | –            | ![Product Image] | 37%       |

$^a$ Yields of isolated products after purification by column chromatography.
NMR spectra for the photoreaction of lignin model substrate 6 (1-(2-methoxyphenoxy)propan-2-one):

Figure S45. Top (green trace): $^1$H NMR spectrum (in CDCl$_3$) of the starting material before photo-irradiation. Bottom (red trace): $^1$H NMR spectrum (in CDCl$_3$) of the isolated product after irradiation of a reaction mixture according to general procedure D, recorded after workup and purification. The C$_{a}$–O bond cleavage product 6-P (22.1 mg, yield 59%) was isolated and purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10/1 ~ 5/1, v/v).
NMR spectra for the photoreaction of lignin model substrate 7 (3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one):

![Substrate Material](image)

**Figure S46.** Top (green trace): $^1$H NMR spectrum (in CDCl$_3$) of the starting material before photo-irradiation. Bottom (red trace): $^1$H NMR spectrum (in CDCl$_3$) of the isolated product after irradiation of a reaction mixture according to general procedure D, recorded after workup and purification. The C$_\alpha$–O bond cleavage product 7-P (16.4 mg, yield 36%) was isolated and purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1 ~ 1/1, v/v).

$^1$H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.95 (d, $J = 9.0$ Hz, 2H), 6.94 (d, $J = 6.9$ Hz, 2H), 4.06 – 3.95 (m, 2H), 3.87 (s, 3H), 3.18 (td, $J = 5.3, 1.7$ Hz, 2H), 2.75 (t, $J = 6.1$ Hz, 1H).
NMR spectra for the photoreaction of lignin model substrate 8 (3-hydroxy-1-(4-hydroxyphenyl)-2-(2-methoxyphenoxy)propan-1-one):

Figure S47. Top (green trace): $^1$H NMR spectrum (in CDCl$_3$) of the starting material before photo-irradiation. Bottom (red trace): $^1$H NMR spectrum (in CDCl$_3$) of the isolated product after irradiation of a reaction mixture according to general procedure D, recorded after workup and purification. The C$_\alpha$−O bond cleavage product 8-P (16.5 mg, yield 40%) was isolated purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1 ~ 1/2, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 7.91 (d, $J$ = 8.6 Hz, 2H), 6.89 (d, $J$ = 8.5 Hz, 2H), 5.39 (s, 1H), 4.02 (dd, $J$ = 11.5, 5.5 Hz, 2H), 3.18 (t, $J$ = 5.3 Hz, 2H), 2.74 (t, $J$ = 6.6 Hz, 1H).
Table S8. Substrate scope of the visible-light-mediated Cα–O bond cleavage.

| Entry | Substrate | Product | Yield⁴ |
|-------|-----------|---------|--------|
| 1     | ![Substrate 1](image1) | ![Product 1](image2) | 62%    |
| 2     | ![Substrate 2](image3) | ![Product 2](image4) | trace  |
| 3     | ![Substrate 3](image5) | ![Product 3](image6) | 59%    |
| 4     | ![Substrate 4](image7) | ![Product 4](image8) | 36%    |
| 5     | ![Substrate 5](image9) | ![Product 5](image10) | 40%    |

⁴ Yields of isolated products after column chromatography.
6. NMR and mass spectra

**Figure S48.** $^1$H-NMR spectrum of PEG$_7$-OTs in CDCl$_3$.

**Figure S49.** $^{13}$C-NMR spectrum of PEG$_7$-OTs in CDCl$_3$.
Figure S50. $^1$H-NMR spectrum of PEG$_7$-N$_3$ in CDCl$_3$.

Figure S51. $^{13}$C-NMR spectrum of PEG$_7$-N$_3$ in CDCl$_3$. 
Figure S52. $^1$H-NMR spectrum of PEG$_7$-NH$_2$ in CDCl$_3$.

Figure S53. $^{13}$C-NMR spectrum of PEG$_7$-NH$_2$ in CDCl$_3$. 
Figure S54. $^1$H-NMR spectrum of PDI(H)-PEG in CDCl$_3$.

Figure S55. $^{13}$C-NMR spectrum of PDI(H)-PEG in CDCl$_3$. 
Figure S56. HR-MS spectrum of PDI(H)-PEG, in the middle panel with PEG chain lengths marked between $n = 5$ ($m/z = 881.3449$) and $n = 9$ ($m/z = 1233.5562$) for [M+Na]$^+$ species. In the bottom panel, $m/z$ peaks for [M–CH$_2$CH$_2$O+2Na]$^{2+}$ species are seen, for example $m/z = 606.2593$ is attributed to the compound with a PEG chain length of $n = 9$. 
**Figure S57.** $^1$H-NMR spectrum of PDI(H)-dipp in CDCl$_3$.

**Figure S58.** $^{13}$C-NMR spectrum of PDI(H)-dipp.
**Figure S59.** Upper panel: experimental HR-MS spectrum of PDI(H)-dipp; lower panel: simulated spectrum.

**Figure S60.** $^1$H-NMR spectrum of PDA-Br in DMSO-d$_6$. 
Figure S61. $^1$H-NMR spectrum of PDI(Br)-PEG in CDCl$_3$.

Figure S62. $^{13}$C-NMR spectrum of PDI(Br)-PEG in CDCl$_3$. 
Figure S63. HR-MS spectrum of PDI(Br)-PEG, in the middle panel with [M+Na]$^+$ species with PEG chain lengths marked between $n = 5$ ($m/z = 995.1382$, $^{79}$Br$^{51}$Br) and $n = 9$ ($m/z = 1391.3742$, $^{79}$Br$^{85}$Br). In the bottom panel, $m/z$ peaks for [M$-$CH$_2$CH$_2$O$+2$Na]$^+$ species are seen, for example the $m/z = 685.1695$ peak is related to the $m/z = 1347.3487$ peak in the middle panel ([M+Na]$^+$), which is due the compound with a PEG chain length of $n = 9$. 

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**Figure S64.** $^1$H-NMR spectrum of PDI(Br)-dipp in CDCl$_3$.

**Figure S65.** $^{13}$C-NMR spectrum of PDI(Br)-dipp in CDCl$_3$. 
Figure S66. Upper panel: experimental HR-MS spectrum of PDI(Br)-dipp; lower panel: simulated spectrum.
Figure S67. \textsuperscript{1}H-NMR spectrum of OED precursor in DMSO-d\textsubscript{6}.

Figure S68. \textsuperscript{13}C-NMR spectrum of OED precursor in DMSO-d\textsubscript{6}.
Figure S69. $^1$H-NMR spectrum of lignin model substrate 4 (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) in CDCl$_3$.

Figure S70. $^{13}$C-NMR spectrum of lignin model substrate 4 (2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethanone) in CDCl$_3$. 
Figure S71. $^1$H-NMR spectrum of lignin model substrate 6 (2-(4-methoxyphenyl)-2-oxoethyl acetate) in CDCl$_3$.

Figure S72. $^{13}$C-NMR spectrum of lignin model substrate 6 (2-(4-methoxyphenyl)-2-oxoethyl acetate) in CDCl$_3$. 
Figure S73. $^1$H-NMR spectrum of lignin model substrate 7 (3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one) in CDCl$_3$.

Figure S74. $^{13}$C-NMR spectrum of lignin model substrate 7 (3-hydroxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-one) in CDCl$_3$. 
Figure S75. $^1$H-NMR spectrum of 4-benzylxoyacetophenone in CDCl$_3$.

Figure S76. $^{13}$C-NMR spectrum of 4-benzylxoyacetophenone in CDCl$_3$. 
Figure S77. $^1$H-NMR spectrum of 4-benzyloxy-α-bromoacetophenone in CDCl$_3$.

Figure S78. $^{13}$C-NMR spectrum of 4-benzyloxy-α-bromoacetophenone in CDCl$_3$.
Figure S79. $^1$H-NMR spectrum of 1-(4-(benzyloxy)phenyl)-2-(2-methoxyphenoxy)ethan-1-one in CDCl₃.

Figure S80. $^{13}$C-NMR spectrum of 1-(4-(benzyloxy)phenyl)-2-(2-methoxyphenoxy)ethan-1-one in CDCl₃.
Figure S81. $^1$H NMR spectrum of 3-hydroxy-1-(4-(benzyl oxygen)phenyl)-2-(2-methoxyphenoxy) propan-1-one in CDCl$_3$.

Figure S82. $^{13}$C NMR spectrum of 3-hydroxy-1-(4-(benzyl oxygen)phenyl)-2-(2-methoxyphenoxy) propan-1-one in CDCl$_3$. 
**Figure S83.** $^1$H NMR spectrum of lignin model substrate 8 (3-hydroxy-1-(4-hydroxyphenyl)-2-(2-methoxyphenoxy)propan-1-one) in CDCl$_3$.

**Figure S84.** $^{13}$C NMR spectrum of lignin model substrate 8 (3-hydroxy-1-(4-hydroxyphenyl)-2-(2-methoxyphenoxy)propan-1-one) in CDCl$_3$. 
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