Synthesis of rigidified flavin–guanidinium ion conjugates and investigation of their photocatalytic properties

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Detailed experimental setups for the photocatalytic experiments

Oxidative photocleavage of dibenzyl phosphate
The photocleavage of dibenzyl phosphate was tested in small glass vials with deuterated solvents (1 mL, MeCN-$d_3$ or D$_2$O), containing the phosphate starting material ($10 \times 10^{-3}$ M) and flavin catalyst ($2 \times 10^{-3}$ M, 20 mol%). The mixture was stirred and irradiated by a LED (440 nm, 5 W) at 40 °C for 2 h (D$_2$O) or 4 h (MeCN-$d_3$), respectively. The products were identified by $^1$H NMR and mass spectrometry and the conversion was determined by integration of the aromatic protons in the $^1$H NMR.

Photoreduction of 4-nitrophenyl phosphate
The photocleavage of dibenzyl phosphate was tested in small glass vials in MeCN or water (5 mL), containing the 4-nitrophenyl phosphate starting material ($10 \times 10^{-3}$ M), triethanol amine as sacrificial electron donor ($100 \times 10^{-3}$ M, 10 equivalents), and flavin catalyst ($1 \times 10^{-3}$ M, 10 mol%). The solution was degassed by three consecutive pump and freeze circles and afterwards, the solution was stirred and irradiated by a LED (440 nm, 5 W) and a UV-lamp (370 nm) at 40 °C for 4 h. Reaction mixtures in MeCN were evaporated and dried. The mixtures of the experiments in water were lyophilized. 4-aminophenyl phosphate and 4-amino phenol as by-product were identified by $^1$H NMR and mass spectrometry, respectively. The conversion was determined by integration of the aromatic protons in the $^1$H NMR.

Photo Diels–Alder-reaction of anthracene with N-methyl-maleinimide
Photoinduced Diels–Alder-reactions were carried out in small glass vials in dry toluene (1.2 mL), containing anthracene ($33 \times 10^{-3}$ M), methyl maleinimide ($83 \times 10^{-3}$ M, 2.5 equivalents), and flavin catalyst ($0.67 \times 10^{-3}$ M, 2 mol%). The mixture was stirred and irradiated by a LED (440 nm, 5 W) at 40 °C for 8 h. Afterwards, the solvent was evaporated and the mixture was dried. The products were identified by $^1$H NMR and mass spectrometry and the conversion was determined by integration of the aromatic protons in the $^1$H NMR.
Calculated gas phase conformations

**Figure S.1:** Calculated conformations of 1 in the gas phase (AM1, Spartan program package).

Figure S.1 shows the two lowest energy conformations of compound 1 in the gas phase (semi-empirical AM1, Spartan program package, difference: 13.5 kJ/mol). It is possible to transform the structures into each other by rotation of the C–C single bonds of the ethane linker that are expected to rotate freely in solution.
UV/Vis and fluorescence spectra of compounds 1, 2 and 3

**Figure S.2:** Absorption spectra of 1, 2 and 3 (MeCN + 1% DMSO, 1 × 10⁻⁵ M)

**Figure S.3:** Fluorescence spectra of 1, 2 and 3 [MeCN + 1% DMSO, 1 × 10⁻⁵ M, excitation at 445 nm (1+2) and 440 nm (3)]
UV- and emission titration of compound 2 and phosphate esters

UV-visible and emission titrations were recorded for compound 2 with sodium phenyl phosphate (dibasic dihydrate) and bis-(4-nitrophenyl) phosphate. UV–visible absorption spectroscopy was performed using a Cary 50 Bio spectrophotometer and fluorescence spectroscopy was performed using a Varian Cary Eclipse fluorescence spectrophotometer. The titration experiments with the phosphate anion species were carried out using a solution (2.5 mL) of compound 2 (50 µM in HEPES Buffer; pH 7.4 and 50 µM in CH₃CN) in a quartz cell at 25 °C. The absorption and emission spectral changes were monitored upon addition of a freshly prepared solution of the analytes (in HEPES Buffer and in CH₃CN) with a microsyringe.

Figure S.4: UV-Visible spectra of compound 2 (a) with bis (4-nitrophenyl) phosphate in CH₃CN, (b) with bis (4-nitrophenyl) phosphate in HEPES Buffer (c) UV-Visible of bis (4-nitrophenyl) phosphate in HEPES Buffer.
**Figure S.5:** UV-Visible spectra of compound 2 and sodium phenyl phosphate (dibasic dihydrate) in HEPES Buffer.

The fluorescence spectroscopic studies of compound 2 are shown below. In the presence of bis-(4-nitrophenyl) phosphate as analyte in acetonitrile the emission intensity decreases, while the change is not prominent in HEPES Buffer solution.

**Figure S.6:** Fluorescence intensity change of compound 2 with bis (4-nitrophenyl) phosphate in CH$_3$CN and in HEPES Buffer. $\lambda_{ex} = 445$ nm, PMT detector voltage is medium, slit width = 5.
With sodium phenyl phosphate (dibasic dihydrate) as the analyte, compound 2 did not show any significant change in its emission intensity.

**Figure S.7:** Fluorescence intensity change of compound 2 with sodium phenyl phosphate (dibasic dihydrate) in HEPES Buffer. $\lambda_{ex} = 445$ nm, PMT detector voltage is medium, slit width = 5.
\(^1\)H NMR spectrum (300 MHz, DMSO-\(d_6\)) (top) and \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)) of compound 6.
$^1$H NMR spectrum (300 MHz, DMSO-$d_6$) (top) and $^{13}$C NMR (75 MHz, DMSO-$d_6$) of compound 9.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) (top) and $^{13}$C NMR (75 MHz, CDCl$_3$) of compound 7.
$^1$H NMR spectrum (300 MHz, CDCl$_3$) (top) and $^{13}$C NMR (75 MHz, CDCl$_3$) of compound 10.
$^1$H NMR spectrum (600 MHz, DMSO-$d_6$) (top) and $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 1.
\(^1\)H NMR spectrum (600 MHz, DMSO-\(d_6\)) (top) and \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) of compound 2.