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Electronic Supplementary Information (ESI) for

Triplet quenching pathway control with molecular dyads enables the identification of a highly oxidizing annihilator class

Maria-Sophie Bertrams,^[a] Katharina Hermainski,^[a] Jean-Marc Mörsdorf,^[b]

Joachim Ballmann,*^[b] and Christoph Kerzig*^[a]

[a] Maria-Sophie Bertrams, Katharina Hermainski, Christoph Kerzig
Department of Chemistry
Johannes Gutenberg University Mainz, Duesbergweg 10-14
55128 Mainz (Germany)
E-mail: ckerzig@uni-mainz.de
[b] Jean-Marc Mörsdorf, Joachim Ballmann
Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 276
69120 Heidelberg, Germany
E-mail: joachim.ballmann@uni-heidelberg.de

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1. General experimental details

1.1 Chemicals

Unless indicated otherwise, chemicals for optical spectroscopy were used as obtained from the supplier (in the highest available purity) without further purification: Ethanol absolute (VWR, >99 %); 9-(methylaminomethyl)anthracene (Sigma-Aldrich, 99 %); Eosin Y disodium salt (Alfa Aesar, 100 weight %); Erythrosin B disodium salt (TCI, >95 %); NaBr (Merck, extra pure 99 %); NaCl (Fisher Chemicals, ≥99.5 %); NaOH (Sigma Aldrich, ≥98 %); perylene (Thermo Scientific, >98 %); disodium 1,5-naphthalenedisulfonate hydrate (TCI, >98 %); PbO₂ (Acros Organic, >97 %); Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium dichloride (Ru(dpp)₃²⁺, Alfa Aesar); Tris(2,2'-bipyridin)ruthenium dichloride × 6 H₂O (Ru(bpy)₃²⁺, Sigma-Aldrich, 99.95 %); Tris(1,10-phenanthroline)ruthenium dichloride × H₂O (Ru(phen)₃²⁺, Sigma-Aldrich, 97 %); Sulfuric acid (Carl Roth, 96 %, VLSI grade).

Tis(1,10-phenanthroline)osmium(II) hexafluorophosphate $(Os(phen)_3^{2+})^1$ was synthetized according to a literature procedure. The dyads $Ru(bpy)_3-xy_1-Ant^{2+}$ (as nitrate salt)², bis(2,2'-bipyridine)(5-pyrenyl-1,10-phenanthroline)ruthenium(II) chloride $(RubpyPy^{2+})^3$ and bis(1,10-phenanthroline)(5-pyrenyl-1,10-phenanthroline)ruthenium(II) chloride $(RuphenPy^{2+})^3$ as well as tris(2,2'-bipyrazine)ruthenium dihexafluorophosphate $(Ru(bpz)_3^{2+})^4$ were available from recent studies.

The solvent used for optical spectroscopy was 50 mM H_2SO_4 in aqueous solution with ultrapure Millipor MilliQ water (specific resistance 18.2 M Ω cm). All solutions for optical spectroscopy were purged with argon (Nippon Gases 5.0) for at least 10 minutes before the measurements and sealed under inert gas in 1.0 cm pathlength septum cap cuvettes (quartz glass).

1.2 Steady-state measurements

Absorption spectra were recorded using a LAMBDA 365 from Perkin Elmer. Emission spectra for the quantum yield determination were measured using a FL 6500 from Perkin Elmer. All steady-state absorption and emission measurements were performed at room temperature (295 ± 2 K) and the emission spectra were corrected for the wavelength-dependent sensitivity of the emission spectrometer. Very low concentrations of the emissive compounds were employed to avoid filter effects. The E_{00} energies were determined from the intersections of the absorption and emission spectra. The fluorescence quantum yields were measured against a known standard compound (perylene in ethanol⁵). To avoid filter effects, the absorbance was adjusted below 0.1 at the excitation wavelengths and in the overlap area of emission and absorption spectra. The quantum yield was then determined according to **Equation S 1**⁵ with Φ ... quantum yield, *I* ... integrated luminescence intensity, *A* ... optical density at the excitation wavelength, and η ... refractive indices of the used solvents. All variables with the index ref correspond to the reference compounds.

$$\boldsymbol{\Phi} = \boldsymbol{\Phi}_{\text{ref}} \times \frac{I}{I_{\text{ref}}} \times \frac{A_{\text{ref}}}{A} \times \frac{\eta^2}{\eta_{\text{ref}}^2}$$

Equation S 1

1.3 Time-resolved measurements

The fluorescence lifetimes of the three annihilator compounds in 50 mM H₂SO₄ were recorded with a mini- τ spectrometer from Edinburgh Instruments (time-correlated single photon counting TCSPC technique), with a pulsed LED (EPLED-300, pulse-width 1020.0 ps, average power 40 μ W, λ_{exc} = 293 nm) or different lasers (EPL-375, pulse-width 58.3 ps, average power 5 mW, λ_{exc} = 371 nm; EPL-450, pulse-width 74.5 ps, average power 5 mW, λ_{exc} = 446 nm) for excitation and the built-in band-pass

filters for detection. For the detection of the 1,5-NDS^{2–} lifetime, a 345 nm long-pass filter from Newport was used. The concentrations of all solutions were adjusted such that the optical density at the excitation wavelength was between 0.1 and 0.2.

For the laser flash photolysis (LFP) measurements an LP980-KS apparatus form Edinburgh Instruments was used. The energy of the 532 nm laser pulse (frequency-doubled Nd:YAG laser from Quantel with ~10 ns pulses) was modified by the Q-switch delay ($50 \mu s - 150 \mu s$, corresponding to energies between 50 mJ and 2.4 mJ, further details are given in the figure captions of the ESI). A beam expander (Thorlabs) was used to ensure homogenous excitation in the detection volume (beam diameter in front of the cuvette window, 0.8 cm). Kinetic traces were recorded at a single wavelength with a photomultiplier tube and for measuring transient absorption (TA) or (delayed) emission spectra an iCCD camera from Andor was employed. All TA spectra were time-integrated for 100 ns. The concentrations of the sensitizers were adjusted such that optical densities at the excitation wavelength between 0.017 and 0.034 resulted (except for Figure S 37, where higher concentrations were used). Exact concentrations are given in the figure captions.

To determine quenching rate constants, Stern–Volmer analyses of the quenching experiments were performed. The τ_0/τ values from LFP or TCSPC studies were plotted against the quencher concentration. A linear fit with the intersection fixed at 1 yielded the Stern–Volmer constant (K_{SV}) and division by the known τ_0 lifetime of the respective excited state under given conditions resulted in the bimolecular quenching rate constant.⁵

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Q] = 1 + k_q \tau_0[Q]$$

Equation S 2

The simulated curves for the quenching efficiencies as a function of the quencher concentrations (Figure 5, main paper) were calculated using deviations of the Stern–Volmer equation. The previously determined quenching rate constants (k_q) and lifetimes without quencher present (τ_0) allowed us to calculate the lifetimes at different quencher concentrations according to **Equation S 3**, which is a rearrangement of the Stern–Volmer equation (**Equation S 2**).

$$\tau = \frac{1}{\frac{1}{\tau_0} + k_q \times [Q]}$$

Equation S 3

The efficiency of the resulting lifetimes was calculated using **Equation S 4**, which can also be derived from **Equation S 2**.

$$\eta = \frac{\tau_0 - \tau}{\tau_0}$$

Equation S 4

1.4 Calculations of excited-state redox potentials

The thermodynamic feasibility of a photo-induced redox reaction (Gibbs energy of photoinduced electron transfer) can be predicted using the following equation⁶

$$\Delta G^{0}_{ET} = E(D^{+/0}) - E(A^{0/-}) - E_{00} - \omega$$

Equation S 5

with $E(D^{*+/0})$... oxidation potential of an electron donor, $E(A^{0/*-})$... reduction potential of an electron acceptor, $E_{0,0}$... the excited state energy of the donor or acceptor, and ω ... the Coulomb-term representative for the Coulombic interactions between two ions, which was neglected in the calculation because the corresponding values are small in water⁶. Potentials from literature were often given vs. SCE and could be adjusted to values vs. NHE by the addition of 0.24 V.⁷ The empirical correlation between ΔG^{0}_{ET} and the observed quenching rate constants was exploited to estimate redox potentials that could not be measured in aqueous solution.^{8,9}

2. Synthetic procedures

2.1 General remarks

All experiments were conducted under an atmosphere of dry and oxygen-free argon by using standard Schlenk techniques. Argon 5.0 was used and further dried by passing over a column of phosphorus pentoxide. Glassware was heated to 130°C overnight and evacuated while still hot. Dichloromethane, diethylether and pentane were purified using an MBraun Solvent Purification System. Deuterated solvents were dried over sodium (C_6D_6 , toluene- d_8) or over calcium hydride (CD_2Cl_2) and distilled prior to use. Chlorodiisopropylphosphine was purified by simple distillation and stored in a Teflon-valve ampule. All other chemicals for synthesis were purchased from commercial suppliers and used as received. 2,2'-Dibromo-tolane¹⁰, 2,2'-dibromo-4,4'-difuorotolane¹¹ and 2,2'-dibromo-4,4'-dichlorotolane¹² were prepared according to literature-known procedures.

One and two dimensional ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker Avance DRX 300, a Bruker Avance II 400 MHz or on a Bruker Avance 600 III spectrometer. Unless noted otherwise, all X-nuclei spectra were recorded with ¹H broadband or composite pulse decoupling. Residual (undeuterated) solvent served as reference for ¹H and ¹³C NMR spectra. Chemical shifts δ are given in parts per million (ppm), coupling constants *J* in Hertz (Hz). Signal multiplicities are stated by common abbreviations (e.g. s – singlet, d – doublet, dd – doublet of doublets).

Mass spectra were recorded at the Department of Organic Chemistry at Heidelberg University on a JEOL JMS-700 magnetic sector by liquid injection FD ionization (LIFDI) technique.

Elemental analyses were carried out at the Department of Inorganic Chemistry at Heidelberg University on an Elementar vario MICRO Cube.

2.2 Synthesis of 2,2'-bis(diisopropylphosphino)tolane derivatives



General procedure: A Schlenk flask was charged with the 2,2'-dibromotolane derivative (1.0 eq, X = H, F, Cl) and dissolved in anhydrous Et_2O . The clear solution was cooled to $-20^{\circ}C$ and "BuLi (2.5 M in hexane, 2.0 eq) was added dropwise over 10 min. The solution was stirred for 20 min at $-20^{\circ}C$ and then placed in an ice bath at 0°C. After 15 min the solution was cooled to $-40^{\circ}C$ and neat chlorodiisopropylphosphine (2.1 eq) was added dropwise. The mixture was allowed to warm to $-20^{\circ}C$ and stirred at this temperature for 2d. The resulting suspension (LiCl precipitate) was filtered over a silica plug under inert atmosphere and the plug was washed with Et_2O , while the filtrate was kept in an ice-bath at 0°C. The filtrate was evaporated under reduced pressure and the residue was

taken up in pentane and filtered over Celite to remove residual amounts of LiCl. The clear filtrate was concentrated under vacuum and the solution was kept at -40° C for crystallization. After 12h, the ensuing colorless crystals were filtered off, washed with a small amount of cold pentane and dried in vacuum. The products are air- and temperature-sensitive, but may be stored indefinitely under an inert atmosphere at -40°C.

Derivative with X=H: This derivative has been reported previously, but the experimental procedure provided here has been improved significantly. The following amounts were used: 4.0 g 2,2'-dibromotolane (11.9 mmol, 1.0 eq) in 120 ml Et₂O, 9.6 ml ^{*n*}BuLi (2.5 M in hexane, 23.6 mmol, 2.0 eq), 4 ml chlorodiisopropylphosphine (25.1 mmol, 2.1 eq). In the silica filtration step, 200 ml Et₂O were needed for washing the silica plug. The product was obtained in 82% yield (4.0 g, 9.8 mmol). The analytical data are in accordance with literature values. ¹H NMR (600 MHz, CD₂Cl₂, 22°C): δ (in ppm) = 7.67-7.63 (m, 2H), 7.49-7.45 (m, 2H), 7.36-7.31 (m, 4H), 2.27 (septd, *J*_{H-P} = 1.0 Hz, *J*_{H-P} = 1.7 Hz, 4H), 1.16 (dd, *J*_{H-H} = 7.0 Hz, *J*_{H-P} = 14.5 Hz, 12H), 0.96 (dd, *J*_{H-H} = 7.0 Hz, *J*_{H-P} = 1.9 Hz, CH), 133.3 (d, *J*_{C-P} = 4.5 Hz, CH), 131.1 (d, *J*_{C-P} = 28.0 Hz, C_q), 128.8 (s, CH), 127.9 (d, *J*_{C-P} = 1.6 Hz, CH), 95.2 (dd, *J*_{C-P} = 10.9 Hz, CH₃). ³¹P{¹H} NMR (243 MHz, CD₂Cl₂, 22°C): δ (in ppm) = 4.9 (s). MS (LIFDI, toluene): Calcd. for C₂₆H₃₆P₂: 410.2292, found: 410.2 [M]⁺. Anal. calcd. for C₂₆H₃₆P₂ (410.52 g/mol): C 76.07, H 8.84, found: C 75.89, H 9.25.

Derivative with X=F: The following amounts were used: 0.6 g 2,2'-dibromo-4,4'-difuorotolane (1.6 mmol, 1.0 eq) in 40 ml of Et₂O, 1.3 ml ⁿBuLi (2.5 M in hexane, 3.2 mmol, 2.0 eq), 5.4 µl chlorodiisopropylphosphine (3.4 mmol, 2.1 eq). In the silica filtration step, 50 ml Et₂O were used for washing the silica plug. The product was obtained in 68% yield (0.5 g, 1.1 mmol). ¹H NMR (600 MHz, C₆D₆, 22°C): δ (in ppm) = 7.67-7.64 (m, 2H), 7.12 (d, J_{H+H} = 9.1 Hz, 2H), 6.65 (td, J = 8.3 Hz, J = 2.6 Hz, 2H), 1.93 (sept, J_{H+H} = 6.9 Hz, 4H), 1.08 (dd, J_{H+P} = 14.4 Hz, J_{H+H} = 7.0 Hz, 12H), 0.86 (dd, J_{H+P} = 11.8 Hz, J_H = 6.9 Hz, 12H). ¹³C{¹H} NMR (151 MHz, C₆D₆, 22°C): δ (in ppm) = 162.2 (d, ¹J_{C+F} = 252 Hz, Cq), 142.5 (dd, J = 26.4 Hz, J = 4.9 Hz, Cq), 135.0 (dd, ³J_{C+F} = 7.8 Hz, ³J_{C+P} = 4.6 Hz, CH), 127.4 (dd, J = 29.7 Hz, J = 3.0 Hz, Cq), 119.4 (d, ²J_{C+F} = 20.6 Hz, CH), 116.0 (d, ²J_{C+F} = 22.1 Hz, CH), 93.9 (d, ³J_{C-P} = 4.9 Hz, Cq), 23.8 (d, ¹J_{C+P} = 15.3 Hz, CH), 20.0 (d, ²J_{C+P} = 18.3 Hz, CH₃), 19.4 (d, ²J_{C+P} = 11.0 Hz, C₄). ¹⁹F{¹H} NMR (376 MHz, C₆D₆, 22°C): δ (in ppm) = -111.8 (m). ³¹P{¹H} NMR (243 MHz, C₆D₆, 22°C): δ (in ppm) = 3.9 (s). MS (EI+): Calcd. for C₂₆H₃₄F₂P₂: 446.2098, found: 446.2089 [M⁺]. Anal. calcd. for C₂₆H₃₄F₂P₂ (446.50 g/mol): C 69.94, H 7.68, found: C 69.87, H 7.94.

Derivative with X=CI: The following amounts were used: 2.5 g 2,2'-dibromo-4,4'-dichlorotolane (5.0 mmol, 1.0 eq) in 120 ml Et₂O, 4.0 ml "BuLi (2.5 M in hexane, 10.0 mmol, 2.0 eq), 1.7 ml chlorodiisopropylphosphine (10.5 mmol, 2.1 eq). In the silica filtration step, 200 ml Et₂O were used for washing the silica plug. The product was obtained in 80% yield (1.9 g, 3.9 mmol). ¹H NMR (400 MHz, C₆D₆, 22°C): δ (in ppm) = 7.57 (dd, J = 8.3 Hz, J = 2.8 Hz, 2H), 7.45 (t, J = 2.1 Hz, 2H), 6.95 (dd, J = 8.3 Hz, J = 2.2 Hz, 2H), 1.92 (hept, J = 6.9 Hz, 4H), 1.05 (dd, J = 14.5 Hz, J = 7.0 Hz, 12 H), 0.85 (dd, J = 11.8 Hz, J = 6.9 Hz, 12H). ³¹P{¹H} NMR (162 MHz, C₆D₆, 22°C): δ (in ppm) = 4.6 (s). MS (EI+): Calcd. for C₂₆H₃₄P₂Cl₂: 478.1507, found: 478.1530 [M⁺]. Anal. calcd for C₂₆H₃₄P₂Cl₂ (479.40 g/mol): C 64.14, H 7.15, found: C 64.08, H 7.39.

2.3 Synthesis of phosphonium-bridged ladder stilbene derivatives



General procedure for the oxidative cyclization with hexachloroethane (X = H, F, Cl): Solid hexachloroethane (1.0 eq) was added to a solution of the 4,4'-substituted (X = H, F, Cl) 2,2'bis(diisopropylphosphino)tolane (1.0 eq) in 50 ml CH₂Cl₂ under an inert atmosphere and the resulting solution was stirred overnight at room temperature. The resulting precipitate was filtered off (in air) and washed with 10 ml CH₂Cl₂. The solid was further washed with a solution of three drops NEt₃ in 10 mL CH₂Cl₂, followed by washing with 10 ml CHCl₃. The solid was dissolved in methanol and crystallized by layering the solution with an equal amount of Et₂O. After a few days, the crystalline yellow product was collected via filtration and dried in vacuum. The fluorescent products were obtained as air-stable (in the solid state) and water-soluble solids.

Derivative with X = H (P-H²⁺): The following amounts were used: 288 mg hexachloroethane (1.22 mmol, 1.0 eq), 500 mg 2,2´-bis(diisopropylphosphino)tolane (1.22 mmol, 1.0 eq). The product was obtained in 97% yield (572 mg, 1.19 mmol). A tree-step synthesis of this compound has been reported previously.¹³ The analytical data are accordance with the literature values. ¹H NMR (D₂O, 600 MHz, 22°C): δ (in ppm) = 8.24-8.21 (m, 2H), 8.03-8.00 (m, 2H), 7.96-7.95 (m, 2H), 7.87-7.86 (m, 2H), 3.69-3.65 (m, 4H), 1.44-1.39 (m, 12H), 1.37-1.33(m, 12H). ¹³C{¹H, ³¹P} NMR (D₂O, 75 MHz, 25°C): δ (in ppm) = 146.7-146.2 (m, C_q), 138.5 (t, J = 12.7 Hz, C_q), 136.9 (s, CH), 134.1 (t, J = 5.5 Hz, CH), 132.4 (t, J = 5.7 Hz, CH), 127.3 (t, J = 3.5 Hz, CH), 120.2-119.5 (m, C_q), 22.6-22.2 (m, CH), 15.2 (bs, CH₃), 14.6 (bs, CH₃). ³¹P{¹H} NMR (D₂O, 243 MHz, 22°C): δ (in ppm) = 58.4 (s). MS (ESI+): Calcd. for C₂₆H₃₇OP₂⁺: 427.2314, found: 427.2315 [M+OH]⁺. Anal. calcd. for C₂₆H₃₆Cl₂P₂ (481.42 g/mol): C 64.87, H 7.54, found: C 64.15, H 7.46.

Derivative with X = F (P-F²⁺): The following amounts were used: 264 mg hexachloroethane (1.12 mmol, 1.0 eq), 500 mg 2,2'-bis(diisopropylphosphino)-4,4'-difluorotolane (1.12 mmol, 1.0 eq). The product was obtained in 95% yield (475 mg, 1.06 mmol). ¹H NMR (400 MHz, D₂O, 22°C): δ (in ppm) = 8.04 - 8.00 (m, 2H), 7.90 (dt, *J* = 8.0 Hz *J* = 3.8 Hz, 2H), 7.69 (td, *J* = 8.6 Hz, *J* = 2.4 Hz, 2H), 3.62 (sept, *J*_{H-H} = 7.2 Hz, 4H), 1.40 - 1.26 (m, 24H). ¹³C{¹H} NMR (151 MHz, D₂O, 22°C): δ (in ppm) = 167.7 - 165.9 (m, C_q), 148.1 - 147.6 (m, C_q), 137.5 - 137.3 (m, C_q), 131.9 (dt, *J* = 9.0 Hz, *J* = 4.0 Hz), 126.4 (d, *J* = 22.9 Hz, CH), 125.5 (d, *J* = 9.0 Hz), 125.1 (t, *J* = 6.2 Hz, CH), 125.0 - 124.8 (m, CH), 25.4 - 25.0 (m, CH), 17.5 (dt, *J* = 87.4 Hz, *J* = 1.4 Hz, CH₃). ¹⁹F{¹H} NMR (376 MHz, D₂O, 22°C): δ (in ppm) = -103.7 (t, *J* = 3.5 Hz). ³¹P{¹H} NMR (162 MHz, D₂O, 22°C): δ (in ppm) = 60.1 (s). MS (ESI+): Calcd. for C₂₆H₃₃F₂P₂: 445.2020, found: 445.2018 [M-H]⁺, calcd. for C₂₆H₃₅F₂OP₂: 463.2126, found: 463.2123 [M+OH]⁺. Anal. calcd. for C₂₆H₃₀Cl₂F₂P₂ × 2 H₂O (553.43 g/mol) C 56.43, H 6.92, found: C 56.35, H 7.19.

Derivative with X = Cl (P-Cl²⁺): The following amounts were used: 232 mg hexachloroethane (0.98 mmol, 1.0 eq). 470 mg 2,2'-bis(diisopropylphosphino)-4,4'-dichlorotolane (0.98 mmol, 1.0 eq). The product was obtained in 87% yield (470 mg, 0.85 mmol). ¹H NMR (400 MHz, D₂O, 22°C): δ (in ppm) = 8.25 (dt, J = 8.3 Hz, J = 2.1 Hz, 2H), 7.98 – 7.96 (m, 2H), 7.84 (dd, J = 8.3 Hz, J = 3.1 Hz, 2H), 3.62 (sept, J = 7.2 Hz, 4H), 1.40 - 1.26 (m, 24H). ¹³C{¹H} NMR (101 MHz, D₂O, 22°C): δ (in ppm) = 145.7 (d, J = 73.5

Hz, C_q), 139.1 (t, J = 7.7 Hz), 137.0 – 136.7 (m), 134.2 (t, J = 6.0 Hz, CH), 128.3 (t, J = 3.8 Hz, CH), 122.1 (d, J = 91.6 Hz, C_q), 23.2 – 22.3 (m, CH), 15.3 (s, CH₃), 14.7 (s, CH₃).³¹P{¹H} NMR (162 MHz, D₂O,22°C): δ (in ppm) = 60.1 (s). MS (ESI+): Calcd. for C₂₆H₃₃Cl₂P₂ [M-H] ⁺: 477.1435, found: 477.1430. Calcd. for C₂₆H₃₅Cl₂OP₂ [M+OH]⁺: 495.1540, found: 495.1533. Anal. Calcd. for C₂₆H₃₄Cl₂P₂ × 3 H₂O (446 g/mol) C 51.67, H 6.67. Found: C 52.09, H 6.54.



3. NMR spectra of the annihilators P-H²⁺, P-F²⁺, P-Cl²⁺

Figure S 1 ¹H NMR spectrum of P-H²⁺(600 MHz, D₂O, 295 K).



Figure S 2 $~^{13}C\{^{1}H\}$ NMR spectrum of P-H2+ (151 MHz, D2O, 295 K).



Figure S 3 ${}^{31}P{}^{1}H$ NMR spectrum of P-H²⁺ (243 MHz, D₂O, 295 K).







Figure S 5 ¹³C{¹H} NMR spectrum of P-F²⁺ (151 MHz, D₂O, 295 K).



Figure S 6 ${}^{31}P{}^{1}H$ NMR spectrum of P-F²⁺ (162 MHz, D₂O, 295 K).



Figure S 7 ${}^{19}F{}^{1}H$ NMR spectrum of P-F²⁺(376 MHz, D₂O, 295 K).







Figure S 9 ¹³C{¹H} NMR spectrum of P-Cl²⁺ (101 MHz, D₂O, 295 K).



Figure S 10 ³¹P{¹H} NMR spectrum of P-F²⁺(162 MHz, D₂O, 295 K).

4. X-Ray crystal structure determinations

Crystal data and details of the structure determinations are compiled in Table S 1. Full shells of intensity data were collected at low temperature with an Agilent Technologies Supernova-E CCD diffractometer (Mo- K_{α} or Cu- K_{α} radiation, microfocus X-ray tube, multilayer mirror optics). Detector frames (typically ω -, occasionally φ -scans, scan width 0.5° for Mo and 1.0° for Cu) were integrated by profile fitting.^{14,15,16} Data were corrected for air and detector absorption, Lorentz and polarization effects^{15,16} and scaled essentially by application of appropriate spherical harmonic functions.^{15–18,19} Absorption by the crystal was treated numerically (Gaussian grid).^{15–20} An illumination correction was performed as part of the numerical absorption correction.^{17,18} Using Olex2²¹, the structures were solved with SHELXT²² (intrinsic phasing) and refined with SHELXL²³ by full-matrix least squares methods based on F^2 against all unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally input at calculated positions and refined with a riding model. The H₂O hydrogen atoms in X = Cl · 1.5 H₂O were located in the difference Fourier map and refined (in part by applying a SADI restraint)

CCDC 2224633 and 2224634 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre's and FIZ Karlsruhe's joint Access Service via https://www.ccdc.cam.ac.uk.

Table S 1 Cryst	al data and details of the	structure determinations fo	or X= F · 4 MeOH and X	= $CI \cdot 1.5 H_2O$.
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Compound	X = F · 4 MeOH	X = CI · 1.5 H ₂ O
Empirical Formula	C ₂₆ H ₃₄ Cl ₂ F ₂ P ₂ , 4 (H ₃ COH)	2 (C ₂₆ H ₃₄ Cl ₄ P ₂), 3 (H ₂ O)
Formula Weight	645.54	1154.59
Crystal system	monoclinic	Triclinic
Space group	P 21/c	<i>P</i> -1
a /Å	7.68726(3)	11.9371(8)
b /Å	16.93199(8)	15.3069(7)
<i>c</i> /Å	13.38321(7)	17.4558(6)
α /°	90	78.259(4)
βl°	94.5657(4)	76.680(4)
μ°	90	69.650(5)
V /ų	1736.440(14)	2883.3(3)
Z	2	2
F ₀₀₀	688	1212
d _c /Mg⋅m ⁻³	1.235	1.330
μ /mm ⁻¹	2.900	0.541
max, min transmission factors	1.000, 0.625	1.000, 0.745
X-ray radiation, λ /Å	Cu- <i>K</i> _α , 1.54184	Mo- <i>K</i> _α , 0.71073
data collect. temperature /K	120(1)	120(1)
heta range /°	4.2 to 71.1	2.4 to 34.2
index ranges <i>h</i> , <i>k</i> , <i>l</i>	±9, ±20, ±16	±18, ±24, –26 to +27
reflections measured	95360	92290
unique [<i>R</i> _{int}]	3356 [0.0315]	22576 [0.0886]
observed $[l > 2\sigma(l)]$	3239	14083
parameters refined [restraints]	199 [0]	644 [1]
GooF on <i>F</i> ²	1.069	1.041
R indices $[I > 2\sigma(I)] R_1$, wR ₂	0.0269, 0.0730	0.0571, 0.1081
R indices (all data) R1, wR2	0.0277, 0.0736	0.1079, 0.1304
difference density: max, min /e·Å⁻³	0.33, -0.23	0.69, -0.48
deposition number CCDC	2224633	2224634



Figure S 11 ORTEP plot of the molecular structure of X = F \cdot 4 MeOH (displacement ellipsoids drawn at 50% probability, CH and CH₃ hydrogen atoms omitted for clarity, only two of the four co-crystallized MeOH molecules are shown for clarity). Selected bond lengths (Å) and angles (°): P-C1 1.7984(12), P-C7 1.7964(12), C1-C1' 1.358(2), C1-C2 1.4663(16), C2-C7' 1.4118(17), C7-P-C1 93.04(6), C1'-C1-P 108.56(11), C1'-C1-C2 117.16(13), C2-C1-P 134.27(9), C7'-C2-C1 111.59(10), C2'-C7-P 109.55(9).



Figure S 12 Packing diagram of $X = F \cdot 4$ MeOH (hydrogen atoms omitted for clarity, view along the b axis).



Figure S 13 ORTEP plot of the molecular structure of X = Cl \cdot 1.5 H₂O (displacement ellipsoids drawn at 50% probability, CH and CH₃ hydrogen atoms omitted for clarity, only one independent molecule and two out of three co-crystallized water molecules are shown for clarity). Selected bond lengths (Å) and angles (°): P1–C1 1.802(2), P2–C2 1.796(2), P1–C8 1.8031(19), P2–C10 1.8069(19), C1–C2 1.366(3), C1–P1–C8 92.40(9), C2–P2–C10 92.38(9), C1–C2–C3 116.66(17), C2–C1–C9 115.97(17), C2–C1–P1 109.12(14), C1–C2–P2 109.76(14). For the two other half-molecules in the asymmetric unit (each completed to a full molecule by symmetry), very similar metrical parameters were found.



Figure S 14 Packing diagram of X=Cl \cdot 1.5 H₂O (hydrogen atoms omitted for clarity, view along the a axis).

5. DFT calculations

The DFT calculations for structure optimization and frequency analysis were carried out with the Gaussian 09 software package²⁴ using the B3LYP functional combined with the 6-311++G(d,p) basis set and the iefpcm model with water as the solvent. No negative vibrational frequencies were observed in the optimized structures indicating the successful convergence on minimum structures. Initially, P-H²⁺ was optimized in its singlet ground state. This structure served as the starting point for the corresponding triplet state calculations and those for the one electron reduced species. The calculated triplet energy, E_{T} (DFT), was determined by comparing the energies of the optimized singlet ground state to that of the corresponding triplet state (Figure S 15), which has been done successfully in previous studies.²⁵

Time-dependent DFT calculations with identical functional and basis set (30 states) were used to calculate the vertical excitation energies for simulating the triplet-triplet absorption spectrum and that of the radical cation. The predicted transitions and their oscillator strengths are displayed in Figure S 16 and Figure S 17. The spin density maps of both species are plotted as insets in the corresponding spectrum, and they were obtained by single point calculations.



Figure S 15 Optimized structures of the $P-H^{2+}$ ground state and the lowest triplet state together with their energy difference, calculated using the B3LYP functional and the 6-311++G(d,p) basis set.



Figure S 16 Spectrum of ${}^{3}P-H^{2+}$ (black) together with the predicted transitions (blue), calculated using TD-DFT with the B3LYP functional and the 6-311++G(d,p) basis set. The inset displays the corresponding spin density map.



Figure S 17 Spectrum of P-H⁺⁺ (black) together with the predicted transitions (blue), calculated using TD-DFT with the B3LYP functional and the 6-311++G(d,p) basis set. The experimental absorption signals above 530 nm correspond to the pure P-H⁺⁺ spectrum. The spectrum below 530 nm is a superposition of P-H⁺⁺ and Ru(bpy)₃³⁺ (with P-H²⁺ and Ru(bpy)₃²⁺ serving as baseline). The inset displays the spin density map calculated for P-H⁺⁺.

6. Quantum yield and lifetime measurements of the annihilators

The lifetimes of the three annihilator compounds were determined in 50 mM H_2SO_4 using the mini- τ apparatus (compare, Section 1). To obtain a high accuracy, the lifetimes were measured under different excitation and detection conditions. The measurements were performed under air and after 10 minutes of argon purging.

P-H²⁺ was exited with the EPL-375 nm and the EPLED-300 nm using filters F3 and F4 of the mini- τ , P-F²⁺ and P-Cl²⁺ were excited with the EPL-375 nm using filters F3 and F4, and EPL-450 nm using filter F4. The resulting lifetimes were averaged and summarized in Table S 2. One sample measurement of each annihilator compound is shown in Figure S 18.

Table S 2Summary of the annihilator lifetimes in 50 mM H_2SO_4 in air-saturated solution and after 10 min of purging with argon.

	P-H ^{2+[a]}	P-F ^{2+[b]}	P-Cl ^{2+[b]}
τ_0 / ns (purged)	14.7 ± 0.09	16.4 ± 0.04	11.4 ± 0.4
τ ₀/ ns (air)	14.5 ± 0.05	16.2 ± 0.1	11.3 ± 0.01

^[a] averaged from measurements upon excitation at 371 nm or 293 nm using filters F3 and F4.

^[b] averaged from measurements upon excitation at 371 nm using filters F3 or F4 and upon excitation at 446 nm using filter F4.



Figure S 18 Left: Emission spectra together with the detection window of the band-pass filters that were used for the lifetime measurements. Right: Sample lifetime measurements of all three annihilator compounds. For each annihilator the sample data set for the excitation with the LED-375 nm combined with detection filter F4 under air and argon are shown.

The fluorescence quantum yields of the annihilator compounds were determined in Ar-saturated 50 mM H_2SO_4 . An Ar-saturated solution of perylene in ethanol (reference quantum yield, 0.92)⁵ was employed as reference. The relative quantum yields were measured at three excitation wavelengths and the absolute values were determined according to **Equation S 1** out of those three measurements.

Table S 3 Summary of fluorescence quantum yields of all annihilator compounds in 50 mM H_2SO_4 after 10 min degassing with argon. The given values are averaged from measurements at three different excitation wavelengths: 380 nm, 408 nm and 418 nm.

Reference compound	P-H ²⁺	P-F ²⁺	P-Cl ²⁺
perylene in ethanol	0.87 ± 0.019	0.85 ± 0.020	0.87 ± 0.023

7. Additional energy- and electron transfer experiments

7.1 Fitting of kinetic absorption and separation of formation and decay kinetics

The quenching rate constants for ET or EnT from the Ru photosensitizers were determined with Stern–Volmer plots. The corresponding kinetic traces were detected at two or three different wavelengths and from the resulting quenching rate constants (k_q) the averaged values are given in the main paper.

The formation of a new species after electron or energy transfer quenching is usually observed at a wavelength where only the newly formed species absorbs, or at an isosbestic point. The TA spectra of the triplet-excited dyads and follow-up species overlap over the entire spectrum and consequently, the kinetic absorption traces always show two superimposed species: Initially the unquenched dyad triplet, which is converted into the less absorbing ³P-H²⁺. Those kinetic traces were fitted using a biexponential function (Figure S 23, detection wavelength 486 nm) to obtain the dyad triplet lifetime under given conditions.

Because the formation kinetics of the EnT product cannot be measured isolated from the initial sensitizer triplet, the contribution of the sensitizer was subtracted from the biexponential decay trace. This was done by normalizing the (isolated) emission kinetic of the sensitizer at a given quencher concentration to the kinetic trace of the absorption at the same quencher concentration. Using the "subtract" function in the program Origin 9, the emission data (Figure S 19, red trace) was subtracted from the absorption data (violet trace), allowing to extract the formation kinetic (blue trace) out of the original absorption trace. A similar separation was carried out for the 3 Ru(phen) ${}^{3^{2+}}$ quenching with P-H²⁺ displayed in Figure S24.



Figure S 19 Example for the process of isolating the formation kinetics of a species (blue trace) from the recorded absorption trace (violet) by subtracting the corresponding emission kinetic trace (red).



Figure S 20 Stern–Volmer ET quenching of 3 Ru(bpy)₃²⁺ by P-H²⁺: The samples with 35 μ M Ru(bpy)₃²⁺ in 50 mM H₂SO₄ were excited at 532 nm using an average pulse energy of 7.5 mJ. The main plots show the kinetic traces at three different detection wavelengths (sensitizer emission at 600 nm, absorption at 455 nm and 475 nm; for the transient absorption (TA) spectra of the sensitizer triplet and the quenching products, see Figure 4 of the main paper), the insets show the corresponding Stern–Volmer plots including the quenching rate constants (k_q).

For a more reliable assignment of the TA bands after ET from ${}^{3}\text{Ru}(\text{bpy})_{3}{}^{2+}$ to P-H²⁺, we independently oxidized Ru(bpy)₃²⁺ (32 μ M) using an acidic (H₂SO₄ 11.0 mL, 0.7 M) solution with PbO₂ (excess) added.²⁶ A simulated Δ OD spectrum of the oxidized Ru(bpy)₃³⁺ (Figure S 21, lower part) shows a bleach in the very same spectral region as has been observed in a delayed TA spectrum of Ru(bpy)₃²⁺ and P-H²⁺ (same figure, middle part). For the assignment of the resulting reduced P-H⁺⁺ species, a UV/vis absorption spectrum of the chemically prepared P-H⁺⁺¹³ was recorded in MeOH (H₂O is impossible for stability reasons) were performed and the resulting spectrum was compared to the delayed TA spectra, which were measured after ET from ${}^{3}\text{Ru}(\text{bpy})_{3}{}^{2+}$ or ${}^{3}\text{Ru}(\text{phen})_{3}{}^{2+}$ (Figure S 22). The overlap of all three (scaled) spectra is excellent for wavelengths above 550 nm (at lower wavelengths, the uncorrected bleach of the oxidized ruthenium species superimposes the spectrum; furthermore, the TA spectra have a P-H²⁺ baseline, whereas the P-H⁺⁺ spectrum was recorded with a solvent baseline, which is why the spectra cannot be compared below 450 nm).



Figure S 21 Upper: Calibrated absorption spectra of $Ru(bpy)_{3}^{3+}$ and $Ru(bpy)_{3}^{2+}$. Middle: Delayed TA spectrum after ET from ${}^{3}Ru(bpy)_{3}^{2+}$ to P-H²⁺ (for experimental conditions, see Figure 4 of the main paper). Lower: Spectral difference between $Ru(bpy)_{3}^{3+}$ and $Ru(bpy)_{3}^{2+}$. The red line serves as a visual aid to follow the bleach observed in the delayed TA spectrum.



Figure S 22 Overlaid spectra of chemically generated P-H^{$\bullet+$} (chemically prepared as in ref.¹³ and with chloride counter ion, the solvent MeOH was refluxed over Mg, distilled and degassed prior to use), and TA spectra after ET from triplet excited Ru-sensitizer (³Ru(bpy)₃²⁺ or ³Ru(phen)₃²⁺) to P-H²⁺; for experimental conditions see main part Figure 4, and Figure S 24.



Figure S 23 Stern–Volmer ET quenching of ³RubpyPy²⁺ by P-H²⁺: The samples with 35 μ M RubpyPy²⁺ in 50 mM H₂SO₄ were excited at 532 nm using an average pulse energy of 8.4 mJ. The main plots show the kinetic traces at three different detection wavelengths (sensitizer emission at 600 nm, absorption at 515 nm and 486 nm; data sets at the latter wavelength were fitted carefully such that the resulting annihilator-derived offsets do not contribute to the initial kinetics; for TA spectra see Figure 4 of the main paper), the insets show the corresponding Stern–Volmer plots including the quenching rate constants (k_q).



7.4 Ru(phen) $_{3}^{2+}$ and P-H²⁺

Figure S 24 Electron transfer reactivity of 3 Ru(phen) ${}_{3}{}^{2+}$ with P-H²⁺, after 532 nm excitation (19.8 mJ) Left: TA spectra of 3 Ru(phen) ${}_{3}{}^{2+}$ (grey, time delay 200 ns) and of oxidized Ru(phen) ${}_{3}{}^{3+}$ and 1.2 mM P-H⁺⁺ after the electron transfer (blue, time delay 2 µs). Right: Kinetic traces of 3 Ru(phen) ${}_{3}{}^{2+}$ (dark grey) and the formation of P-H⁺⁺ (blue, subtracted kinetic trace).



Figure S 25 Stern–Volmer ET quenching of ${}^{3}Ru(phen)_{3}{}^{2+}$ by P-H²⁺: The samples with 24 μ M Ru(phen)₃²⁺ in 50 mM H₂SO₄ were excited at 532 nm using an average pulse energy of 14.6 mJ. The main plots show the kinetic traces at three different detection wavelengths (sensitizer emission at 600 nm, absorption at 450 nm and 470 nm, for corresponding TA spectra see Figure S 24), the insets show the resulting Stern–Volmer plots including the quenching rate constants (k_{α}).



7.5 Ru(phen) $_3^{2+}$ and P-F²⁺ or P-Cl²⁺

Figure S 26 Quenching of 3 Ru(phen)₃²⁺ by P-Cl²⁺ (blue) and P-F²⁺ (green, same color-code throughout the figure, all measured with λ_{exc} = 532 nm, 25 mJ) with preliminary Stern–Volmer plots (left), the TA spectra of 3 Ru(phen)₃²⁺ (black) and with one of the annihilators present (all after a time delay of 2 µs). The right part of the figure contains the kinetic traces for the quenching of 3 Ru(phen)₃²⁺ with the two annihilators; the same solutions as for the TA spectra were used.

7.6 RuphenPy²⁺ and P-H²⁺



Figure S 27 Energy transfer reactivity of ³RuphenPy²⁺ with P-H²⁺ (initial concentrations 39 μ M RuphenPy²⁺, 0.3 mM P-H²⁺) after 532 nm excitation (14.6 mJ). Left: TA spectra of ³RuphenPy²⁺ (black, time delay 100 ns) and ³P-H²⁺ after the energy transfer (red, time delay 15 μ s). Right: Kinetic traces (λ_{exc} = 532 nm, 8.4 mJ) of ³RuphenPy²⁺ without (black) and with 0.3 mM P-H²⁺ added to the solution (red).



Figure S 28 Stern–Volmer EnT quenching of ³RuphenPy²⁺ with P-H²⁺: The samples with 39 μ M RuphenPy²⁺ in 50 mM H₂SO₄ were excited at 532 nm using an average pulse energy of 8.4 mJ. The main plots show the kinetic traces at two different detection wavelengths (absorption 515 nm and 481 nm, for corresponding TA spectra see Figure S 27), the insets show the resulting Stern–Volmer plots including the quenching rate constants (k_q).

7.7 Ru(bpz)₃²⁺ and P-H²⁺



Figure S 29 Energy transfer reactivity of 3 Ru(bpz) $_{3}^{2+}$ (46 μ M) with P-H²⁺ (7.1 mM) after 532 nm excitation (25 mJ). TA spectra of 3 Ru(bpz) $_{3}^{2+}$ (black, time delay 200 ns) and 3 P-H²⁺ (red, time delay 4 μ s) after the energy transfer are shown.



Figure S 30 Stern–Volmer EnT quenching of 3 Ru(bpz)₃²⁺ by P-H²⁺: The samples with 20 μ M Ru(bpz)₃²⁺ in H₂O were excited at 532 nm using an average pulse energy of 25 mJ. The main plots show the kinetic traces at two different detection wavelengths (sensitizer emission at 600 nm and TA at 470 nm, corresponding TA spectra are shown in Figure S 29), the insets show the resulting Stern–Volmer plots including the quenching rate constants (k_q).

Non-coordinated heteroatoms of the bipyrazine ligands can be protonated, which leads to a shift in the UV/vis absorption, and a change in optical properties.²⁷ For that reason, all measurements involving $Ru(bpz)_3^{2+}$ were performed in neat H₂O (MillliQ). To estimate the kinetic salt effect caused by the addition of 50 mM H₂SO₄, which is present in all other solutions and serves as ionic strength buffer due to the high degree of acid dissociation, we compared the EnT quenching constants of the dyads RuphenPy²⁺ and RubpyPy²⁺ in pure water with those measured in 50 mM H₂SO₄ (see main paper Table 1). EnT between the two cationic species is faster in the acidic solution and the resulting factor is similar.

Table S 4 Rate constants (k_q) for EnT quenching of ${}^{3}[Ru]^{2+}$ with P-H²⁺ in neat water and 50 mM H₂SO₄.

	RuphenPy ²⁺	RubpyPy ²⁺	Ru(bpz) ₃ ²⁺
<i>k</i> _q (H ₂ O) / 10 ⁹ M ⁻¹ s ⁻¹	0.47	0.63	0.09
<i>k</i> _q (H₂SO₄ 50 mM) / 10 ⁹ M ⁻¹ s ⁻¹	1.44	1.50	≈0.25
factor	3.06 ^[a]	2.38 ^[a]	2.72 ^[b]

^[a] k_q (H₂O) × factor = k_q (H₂SO₄ 50 mM)

^[b] averaged from dyads.

7.8 Quenching studies with further photosensitizers

The following table contains the additional sensitizers that have been tested with the quencher $P-H^{2+}$, along with their triplet energies and calculated quenching efficiencies under our experimental conditions. Key observations are summarized and explained in more detail in the following paragraphs. The concentrations of the metal-based sensitizers were chosen such that the absorption at the excitation wavelength 532 nm was between 0.02-0.03 and for the organic dyes the absorption was set to 0.2.

Table S 5 Literature known photosensitizers together with their triplet energies, the calculated efficiencies for the excitedstate quenching with $P-H^{2+}$ (in Ar-saturated H_2O) and the spectral changes observed after quenching.

Sensitizer ^[a]	<i>E</i> ⊤/ eV	$\eta_{q^{[b]}}$ ([P-H ²⁺] / mM)	Observation ^[a]
Os(phen) ₃ ²⁺	1.8 ²⁸	0.18 (5.0)	ET, bleach indicating Os ³⁺ formation
Rubpy-xy-Ant ²⁺	~ 1.84 ²	>0.99 (1.2)	ET, bleach indicating Ru ³⁺ formation
Ru(dpp)₃²+	2.0-2.2 ²⁹	0.74 (1.2)	ET, bleach indicating Ru ³⁺ formation
Eosin Y (EY ²⁻)	1.9 ³⁰	>0.99 (0.6)	ET, absorption of EY ^{•–} and bleach for EY ^{2–}
Erythrosin B (ETB ²⁻)	1.8-2.0 ³¹	>0.99 (0.3)	ET, absorption of ETB ^{•–} and bleach for ETB ^{2–}

^[a] For chemical structures of the sensitizers, corresponding spectra and kinetic traces see Figure S 31 - Figure S 35.

^[b] Under our experimental conditions: In Ar-saturated H₂O, concentration of the quencher P-H²⁺ is given in brackets.

Os(phen)₃²⁺ + P-H²⁺



Figure S 31 Left: Emission decay traces of ${}^{3}Os(phen)_{3}{}^{2+}$ without (black trace) and with 5.0 mM P-H²⁺ (blue trace) together with the structure of the sensitizer (all solutions were measured in Ar-saturated H₂O, after excitation with 532 nm, 30 mJ); Middle: TA spectrum of the Os(phen)_{3}{}^{2+} P-H²⁺ (5.0 mM) solution after 600 ns time delay; Right: (*)Picture taken from ref. ³², with the simulated (purple trace) and measured (green trace) spectrum of Os(bpy)_{3}{}^{3+}.

Excited ${}^{3}Os(phen)_{3}{}^{2+}$ is evidently quenched by P-H²⁺ and the TA spectrum after quenching shows a bleach between 450-530 nm (Figure S 31). P-H²⁺ does not absorb in that spectral region and the

corresponding triplet would show a positive absorption band (main part, Figure 4). Therefore, the bleach can be unambiguously assigned to the oxidized Os-species³² (right part of Figure S 31) originating from oxidative quenching of ${}^{3}Os(phen)_{3}{}^{2+}$ by P-H²⁺ (ET reactivity).





Figure S 32: Left: TA spectra of ³Rubpy-xy-Ant²⁺ (black)² and the sensitizer with 1.2 mM of P-H²⁺ added (blue), after a 4 μ s time delay (after 532nm excitation, 30 mJ); Upper right: Structure of the sensitizer; Lower right: TA measurement of the sensitizer (green) with 1.2 mM of P-H²⁺ detected at 570 nm.

The quenching product for the system ${}^{3}Rubpy-xy-Ant^{2+}$ (whose initial ${}^{3}MLCT$ is converted to triplet anthracene on a sub-nanosecond timescale)² and P-H²⁺ has a broad absorption above 500 nm, which strongly resembles the spectrum of the reduced P-H⁺ species (Figure S 17 and Figure S 22). The maximum at 570 nm is essentially identical to the one observed for electron transfer reactions with ${}^{3}Ru(bpy)_{3}{}^{2+}$ (see main part Figure 4) or ${}^{3}Ru(phen)_{3}{}^{2+}$ (Figure S 24). The absence of the ${}^{3}P-H^{2+}$ absorption maximum provided further evidence that the dyad ${}^{3}Rubpy-xy-Ant^{2+}$ reduces the P-H²⁺ and does not undergo energy transfer but rather an electron transfer as main quenching pathway.

 $Ru(dpp)_{3}^{2+} + P-H^{2+}$



Figure S 33 Upper left: Emission decay of 3 Ru(dpp) ${}_{3}{}^{2+}$ without (black trace) and with 1.2 mM P-H²⁺ added (after 532 nm excitation, 30 mJ); same color code throughout the figure; Lower left: Absorption decay traces detected at 465 nm; Right: TA spectra of 3 Ru(dpp) ${}_{3}{}^{2+}$ (black) and after the quenching with P-H²⁺ (time delay10 µs indicated by red boxes in the kinetic traces of the left part of the figure), together with the structure of the sensitizer.

The kinetic traces of absorption and emission show quenching of ${}^{3}Ru(dpp)_{3}{}^{2+}$ by P-H²⁺. The bleach at 465 nm in the TA spectrum after quenching can be assigned to the oxidized Ru-species (compare Figure 4 main part and Figure S 24 and Figure S 21). This, together with the absence of the ${}^{3}P-H^{2+}$

absorption band (expected in the same spectral region, around 470 nm), points to an electron transfer reaction between ${}^{3}Ru(dpp)_{3}{}^{2+}$ and P-H²⁺.

EY²⁻ + P-H²⁺



Figure S 34 Left: TA spectrum of EY^{2-} (black, scaled, structure shown as inset) and post-quenching spectrum with P-H²⁺ (0.6 mM, blue), after excitation with 532 nm, 30 mJ; Upper right: Kinetic absorption trace for the formation of the oxidized form EY^{--} ; Lower right:^(*) TA spectra at different delay times taken from³³, which show the formation of EY^{--} in the presence of an oxidative quencher (NB = nitrobenzene, in H₂O:EtOH mixture).

The oxidized form of EY^{2-} shows two significant transient signatures: the bleach around 515 nm and a new absorption band around 460 nm.^{33,34} Both bands are also observed in our quenching studies (left part of Figure S 34) with P-H²⁺, confirming an electron transfer between the excited EY^{2-} and P-H²⁺.

ETB²⁻ + P-H²⁺



Figure S 35 Left: TA spectra of ETB^{2-} without (black, scaled) and with (blue) P-H²⁺ after quenching, in Ar-saturated H₂O, excitation with 532 nm pulses, 30 mJ; Right: Structure of the photosensitizer Erythrosin B (ETB^{2-}).

As observed for the structurally related EY^{2-} , the quenching product of ${}^{3}ETB^{2-}$ with P-H²⁺ shows the ground state bleach (530 nm) and a new absorption band in the blue/green spectral region (480 nm). Owing to the similarity of EY^{2-} and ETB^{2-} (identical structure, only the bromo substituents have been replaced by iodine), and again the lack of the absorption band of ${}^{3}P-H^{2+}$ despite high quenching efficiencies, we conclude that an electron transfer between the excited ETB^{2-} and $P-H^{2+}$ takes place.

8. Additional sTTA experiments

8.1 RubpyPy²⁺ and P-H²⁺



Figure S 36 Top: Reaction scheme of sTTA with RubpyPy²⁺ (22 μ M) and P-H²⁺ (1.2 mM). Left: Time-gated emission spectra (excitation at λ = 532 nm, 25 mJ) of ³RubpyPy²⁺ and ¹P-H^{2+*} (black, delay 250 ns integrated over 300 μ s), the isolated spectrum after sTTA (blue, delay 7 μ s integrated over 300 μ s). The control measurement with only P-H²⁺ in solution after 532 nm excitation (no emission observed) is shown in Figure 6 of the main paper. Right: Relative kinetic traces (excitation at λ = 532 nm, 27 mJ) of ³RubpyPy²⁺ with 1.2 mM P-H²⁺ (black, λ_{det} = 600 nm), formation of ³P-H²⁺ (red, λ_{det} = 470 nm, subtracted kinetic trace, for details see page S19-S20) and the formation and decay of ¹P-H^{2+*} after sTTA (blue, λ_{det} = 500 nm).



8.2 Ru(bpz) $_{3}^{2+}$ and P-H²⁺

Figure S 37 Top: Reaction scheme of sTTA with Ru(bpz)₃²⁺ (80 μ M) and P-H²⁺ (8.3 mM) in neat water. Left: Time-gated emission spectra (excitation at λ = 532 nm, 25 mJ) of ³Ru(bpz)₃²⁺ (black, delay 50 ns integrated over 100 ns), the isolated spectrum after sTTA (blue, delay 6 μ s integrated over 500 μ s). Right: Normalized kinetic traces (excitation at λ = 532 nm, 25 mJ) of ³Ru(bpz)₃²⁺ with 10 mM P-H²⁺ (black, λ_{det} = 600 nm) and formation of ³P-H²⁺ (red, [a] λ_{det} = 470 nm, subtracted kinetic trace, for details see page S19-S20).

8.3 RuphenPy²⁺ and P-H²⁺



Figure S 38 Comparison of direct (reference, grey data sets for 26 μ M RuphenPy²⁺) sensitizer emission and delayed annihilator emission after sTTA (blue data sets, 26 μ M RuphenPy²⁺ and 511 μ M P-H²⁺) at different excitation intensities. Upper left: Normalized emission of the sensitizer RuphenPy²⁺ as reference, almost linear intensity dependence (right plot, the exponent of the power function is 0.89). Lower left: Normalized emission of ¹P-H^{2+*} after sTTA-UC. The intensity dependence is almost quadratic (right plot, the exponent of the power function is 1.72).





Figure S 39 Upper panel: Energy transfer quenching between ³RuphenPy²⁺ (52 μ M) and P-F²⁺ after excitation at λ = 532 nm (46 mJ for spectra, 20 mJ for kinetics); left, kinetic traces of the ³RuphenPy²⁺ emission with increasing P-F²⁺ concentrations; right, Stern–Volmer plot resulting in k_q = 1.07 × 10⁹ M⁻¹s⁻¹. Lower panel, left: TA spectra of ³RuphenPy²⁺ and ³P-F²⁺ before and after EnT; right: Emission spectra of ³RuphenPy²⁺ without P-F²⁺ (time delay 50 ns, black), and ³RuphenPy²⁺ with 0.27 mM P-F²⁺ after 50 ns time delay (dark violet), and the isolated emission after sTTA, with a time delay of 50 µs (light violet). All emission spectra were integrated over 200 µs.



Figure S 40 Upper panel: Energy transfer quenching between ³RuphenPy²⁺ (initial sensitizer concentration 17 μ M) and P-Cl²⁺ after excitation at λ = 532 nm (25 mJ for spectra, 20 mJ for kinetics); left, kinetic traces of the ³RuphenPy²⁺ emission with increasing P-Cl²⁺ concentrations; right, Stern–Volmer plot resulting in k_q = 1.30 × 10⁹ M⁻¹s⁻¹. Lower panel, left: TA spectra of ³RuphenPy²⁺ and ³P-Cl²⁺ (after EnT); right: Emission spectra of ³RuphenPy²⁺ without P-Cl²⁺ (time delay 50 ns, black) and the isolated emission after sTTA, with a time delay of 25 μ s and with 0.3 mM P-Cl²⁺ (turquoise trace).

8.5 Comparison UC vs. direct emission



Figure S 41 Comparative ¹P-H^{2+*} emission spectra upon direct excitation in diluted solution (blue spectrum, measured on the FL6500; in 50 mM H₂SO₄, λ_{exc} = 386 nm, 1.9 μ M P-H²⁺), and at the concentration used for sTTA (red spectrum, measured on the FL6500; in 50 mM H₂SO₄, λ_{exc} = 355 nm, 1.2 mM P-H²⁺), together with the delayed emission after sTTA with the corresponding sensitizer (green spectrum, measured on the LP980 setup (detection with iCCD camera, in 50 mM H₂SO₄, λ_{exc} = 532 nm, 8.4 mJ, 26 μ M RubpyPy²⁺ and 1.2 mM P-H²⁺).

As a proof for no natural triplet formation, the annihilator structure was excited directly (355 nm) and TA as well as delayed emission spectra were measured. Both did not show any signals, which is why the observed emission with the complete UC system and the TA signals can only result from sensitization. For comparison, the spectra after ET or EnT are given in Figure S 42.



Figure S 42 Control measurements of the annihilator $P-H^{2+}$ without (gray spectrum, 355 nm excitation, 14 mJ) or with either of the photosensitizers RuphenPy²⁺ (red) or Ru(bpy)₃²⁺ (blue) in 50 mM H₂SO₄. Left: TA spectrum of only P-H²⁺ with a time delay of 100 ns (grey), and under sensitization conditions for the ET and EnT processes as detailed in Figure S 24 and Figure S 27. Right: delayed emission spectra of the pure annihilator solution (gray, time delay 250 ns, integrated over 800 μ s, 355 nm excitation), a spectrum after sTTA (red, RuphenPy²⁺ 26 μ M, excitation at 532 nm with 8.4 mJ, time delay 20 μ s, integrated over 250 μ s), and a spectrum of Ru(phen)₃²⁺ (24 μ M) and 1.2 mM P-H²⁺ after 532 nm excitation (integrated over 100 μ s, time delay 100 ns).

9. Cl⁻ as reductive quencher

This section contains the raw data sets and resulting Stern–Volmer plots for the chloride quenching of directly excited water-soluble annihilators. The summary of the corresponding rate constants is given in the main paper (Table 2). All experiments were conducted after 10 min purging with argon gas.

The solutions for MAMA⁺, P-Cl²⁺, P-F²⁺ and P-H²⁺ were prepared in 50 mM H₂SO₄, thereby ensuring identical ionic strengths of the solutions. For 1,5-NDS²⁻, we selected 50 mM NaOH to avoid the protonation of sulfonate groups, which would change the redox potentials that are literature-known for the dianion drastically. To get insights into the kinetic salt effects that strongly depend on the charge of the ionic emitter, 1,5-NDS²⁻ was measured in pure H₂O and in 50 mM NaOH. The effective Coulombic repulsion between the dianion 1,5-NDS²⁻ and the chloride is reduced at higher ionic strengths, which would accelerate the quenching kinetics. 1,5-NDS²⁻ is clearly not quenched by chloride, regardless of the ionic strength of the solution.

At very high quencher concentrations, the Stern–Volmer plots show either a downward or an upward curvature. This is due to additional kinetic salt effects caused by the ionic quencher, which accelerate (e.g. in Figure S 53) or decelerate (e.g. in Figure S 43) the second-order rate constants, depending on the charge of the emitter. For the rate constant determinations, only the linear regions of the Stern–Volmer plots have been used.



Figure S 43 Left: Kinetic emission traces of ¹P-H^{2+*} with increasing NaCl concentrations in 50 mM H₂SO₄, after 371 nm excitation. Right: Resulting Stern–Volmer plot. See Figure S 18 for the spectrum of filter F3 in the detection path.



Figure S 44 Left: Stern–Volmer plot (upper) and sample kinetic traces (lower) for ${}^{1}P-F^{2+*}$ quenching by NaCl in 50 mM H₂SO₄. Only two kinetic traces (without NaCl and with 198.1 mM NaCl) are shown for better visibility. Right: Stern–Volmer plot (upper) and sample kinetic traces (lower) for ${}^{1}P-Cl^{2+*}$ quenching by NaCl in 50 mM H₂SO₄. Only two kinetic traces (without NaCl and with 199.3 mM NaCl) are shown for better visibility. See Figure S 18 for the spectra of filters F3 and F4 that were used in the detection path. Excitation occurred at 371 nm.

9.2 P-F²⁺ and P-Cl²⁺

9.3 Cl⁻-quenching with literature-known annihilators



Figure S 45 Left: Kinetic emission traces of 1,5-NDS^{2-*} in 50 mM aqueous NaOH with (pink) and without (black) NaCl added. Right: Kinetic emission traces of 1,5-NDS^{2-*} in pure H₂O without (black) and with different concentrations of NaCl (color-coded data sets) added.



Figure S 46 Kinetic emission traces of ${}^{1}MAMA^{**}$ without (black) and with NaCl (different concentrations, color-coded) added. The solutions were prepared in 50 mM H₂SO₄ and excited at 371 nm.

9.4 Cl⁻ quenching after sTTA

Figure S 47 indicates that quenching with chloride ions is similarly possible after annihilation. All data sets in the figure follow the same color code with the black spectra or kinetic traces referring to the upconversion system without chloride ions as quencher, whereas the red spectra and kinetic traces correspond to solutions with chloride as quencher added. The triplet is essentially unaffected by the presence of the quencher (see kinetic traces on the left side of the figure, detection at 471 nm). Similarly, the rise and decay kinetics of the delayed emission do not change upon NaCl addition (lower right part of the figure). However, a significant decrease of the delayed emission intensity is observed (upper right part of the figure). The impact of Cl⁻ on the emission intensity after sTTA resembles that of the direct (lifetime) quenching of ¹P-H^{2+*}.



Figure S 47 Quenching of chloride after sTTA: The two solutions, with chloride (red data) added as quencher or without the quencher (black data) in 50 mM H_2SO_4 , were investigated under identical measuring conditions (Ruphen²⁺ 30 μ M, P-H²⁺ 540 μ M, excited with 532 nm, 50 mJ). The kinetic traces of the ³P-H²⁺ (left part, detection at 471 nm, compare TA-spectra of Figure S 27) show an identical intensity regardless of the presence or absence of the quencher. The inset shows the kinetic traces after subtraction of the initial sensitizer signals. Also, the duration of the delayed emission (kinetic traces lower right part) is not affected by the presence or absence of NaCl. Upper right: Spectra of delayed ¹P-H^{2+*} emission, delayed 10 μ s and integrated over 70 μ s.

10. Br⁻ as reductive quencher

This section contains the raw data sets and resulting Stern–Volmer plots for the bromide quenching of directly excited, water-soluble annihilators. The singlet states of our novel annihilators ${}^{1}P-H^{2+*}$, ${}^{1}P-F^{2+*}$, and ${}^{1}P-Cl^{2+*}$ are all quenched with diffusion-controlled kinetics by bromide, whereas the rate constants of literature-known annihilators are clearly below the diffusion limit. The summary of the corresponding rate constants is given in the main paper (Table 2). All experiments were conducted after 10 min purging with argon gas. The same considerations as for chloride quenching (see above) hold true regarding the selected additives and salt effects.



Figure S 48 Kinetic emission traces of ${}^{1}P-H^{2+*}$ (black) with increasing NaBr concentrations in 50 mM H₂SO₄, after 371 nm excitation. Right: Stern–Volmer plot of ${}^{1}P-H^{2+*}$ quenching by NaBr together with the resulting quenching rate constant. See Figure S 18 for the spectrum of filter F3 in the detection path.



Figure S 49 Kinetic emission traces of $^{1}P-F^{2+*}$ (black) with increasing NaBr concentrations in 50 mM H₂SO₄, after 371 nm excitation. Right: Stern–Volmer plot of $^{1}P-F^{2+*}$ quenching by NaBr together with the resulting quenching rate constant. See Figure S 18 for the spectrum of filter F4 in the detection path.



Figure S 50 Kinetic emission traces of ¹P-Cl^{2+*} (black) with increasing NaBr concentrations in 50 mM H₂SO₄, after 371 nm excitation. Right: Stern–Volmer plot of ¹P-Cl^{2+*} quenching by NaBr together with the resulting quenching rate constant. See Figure S 18 for the spectrum of filter F4 in the detection path.



Figure S 51 Kinetic emission traces of 1 1,5-NDS^{2-*} (black) in 50 mM NaOH with increasing NaBr concentrations, after 293 nm excitation using a 345 nm long-pass filter to exclude excitation stray light. Right: Stern–Volmer plot of 1 1,5-NDS^{2-*} quenching by NaBr together with the resulting quenching rate constant.



Figure S 52 Kinetic emission traces of 1 1,5NDS^{2-*} (black) in H₂O with increasing NaBr concentrations, after 293 nm excitation using a 345 nm long-pass filter to exclude excitation stray light. Right: Stern–Volmer plot of 1 1,5NDS^{2-*} quenching by NaBr together with the resulting quenching rate constant.



Figure S 53 Kinetic emission traces of ${}^{1}MAMA^{+*}$ (black) with increasing NaBr concentrations in 50 mM H₂SO₄, after 371 nm excitation. Right: Stern–Volmer plot of ${}^{1}MAMA^{+*}$ quenching by NaBr together with the resulting quenching rate constant.

11. Quenching of ¹P-H^{2+*} with 1,5-NDS²⁻

Further quenching experiments were performed for a more precise estimation of the (excited state) reduction potential of P-H²⁺. The water-soluble naphthalene 1,5-NDS²⁻ with known oxidation potential ($E(NDS^{\bullet-/2-}) = 2.03 \text{ V } vs. \text{ NHE}^{35}$) was used in acidic 1,5-NDS²⁻ solution. However, the solubility of 1,5-NDS²⁻ at 50 mM H₂SO₄ is insufficient, which is why this quenching experiment was performed in diluted sulfuric acid (1 mM, see Figure S 54).



Figure S 54 Kinetic traces of ${}^{1}P-H^{2+*}$ without (black) and with 1,5-NDS²⁻ (different concentrations) after 371 nm excitation in 1 mM H₂SO₄. Right: Corresponding Stern–Volmer-plot together with the resulting quenching rate constant.

12. References

- 1 Y. Wei, Y. Li, M. Zheng, X. Zhou, Y. Zuo and C. Yang, Adv. Opt. Mater., 2020, 8, 1902157.
- 2 S. Neumann, O. S. Wenger and C. Kerzig, *Chem. Eur. J.*, 2021, 27, 4115–4123.
- 3 A. C. Sell, J. C. Wetzel, M. Schmitz, A. W. Maijenburg, G. Woltersdorf, R. Naumann and C. Kerzig, *Dalton Trans.*, 2022, **51**, 10799–10808.
- 4 F. M. Hörmann, C. Kerzig, T. S. Chung, A. Bauer, O. S. Wenger and T. Bach, *Angew. Chem. Int. Ed.*, 2020, **59**, 9659–9668.
- 5 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of photochemistry*, CRC/Taylor & Francis, Boca Raton, 3rd edn., 2006.
- 6 G. J. Kavarnos and N. J. Turro, Chem. Rev., 1986, 86, 401–449.
- 7 N. Elgrishi, K. J. Rountree, B. D. McCarthy, E. S. Rountree, T. T. Eisenhart and J. L. Dempsey, J. Chem. Educ., 2018, **95**, 197–206.
- 8 D. Rehm and A. Weller, Isr. J. Chem., 1970, 8, 259–271.
- 9 S. Farid, J. P. Dinnocenzo, P. B. Merkel, R. H. Young, D. Shukla and G. Guirado, *J. Am. Chem. Soc.*, 2011, **133**, 11580–11587.
- 10 A. Orita, N. Yoshioka, P. Struwe, A. Braier, A. Beckmann and J. Otera, *Chem. Eur. J.*, 1999, **5**, 1355–1363.
- 11 H.-K. Chang, S. Datta, A. Das, A. Odedra and R.-S. Liu, *Angew. Chem. Int. Ed.*, 2007, **46**, 4744–4747.
- J. Nejedlý, M. Šámal, J. Rybáček, I. G. Sánchez, V. Houska, T. Warzecha, J. Vacek, L. Sieger, M. Buděšínský, L. Bednárová, P. Fiedler, I. Císařová, I. Starý and I. G. Stará, *J. Org. Chem.*, 2020, **85**, 248–276.
- 13 P. Federmann, H. K. Wagner, P. W. Antoni, J.-M. Mörsdorf, J. L. Pérez Lustres, H. Wadepohl, M. Motzkus and J. Ballmann, *Org. Lett.*, 2019, **21**, 2033–2038.
- 14 K. Kabsch, in Rossmann and M. G. Arnold, eds., *"International Tables for Crystallography"*, Vol. F, Ch. 11.3, Kluwer Academic Publishers, Dordecht, The Netherlands, 11th edn., 2001.
- 15 Rigaku Oxford Diffraction, Rigaku Polska Sp.z.o.o., Worclaw, 2015-2020.
- 16 CrysAlisPro, Agilent Technologies UK Ltd., Oxford, UK, 2011-2014.
- 17 SCALE3 ABSPACK. CrysAlisPro, Agilent Technologies UK Ltd., 2011-2014.
- 18 Rigaku Oxford Diffraction, Rigaku Polska Sp.z.o.o., Poland, 2015-2020.
- 19 R. H. Blessing, Acta. Cryst., 1995, A51, 33-38.
- 20 W. R. Busing and H. A. Levy, Acta. Cryst., 1957, 10, 180–182.
- 21 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
- 22 a) G. M. Sheldrick, SHELXT, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany, 2012-2018; b) M. Ruf and B. C. Noll, Application Note SC-XRD 503, Bruker AXS GmbH, Karlsruhe, Germany, 2014; c) G. M. Sheldrick, Acta. Cryst., 2015, A71, 3–8.
- 23 a) G. M. Sheldrick, *Acta. Cryst.*, 2008, A64, 112–122; b) G. M. Sheldrick, *Acta. Cryst.*, 2015, C71, 3–8; c) G. M. Sheldrick, *SHELXL-20xx*, University of Göttingen and Bruker AXS GmbH, Karlsruhe, Germany, 2012-2018.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani,
 V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R.
 Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-

Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian, Inc.*, Gaussian, Inc., Wallingford CT, 2016.

- 25 a) C. Fischer, C. Kerzig, B. Zilate, O. S. Wenger and C. Sparr, ACS Catal., 2010, 10, 210–215; b) V. Gray, A. Dreos, P. Erhard, B. Albinsson, K. Moth-Poulsen and M. Abrahamsson, Phys. Chem. Chem. Phys., 2017, 19, 10931–10939; c) L. Vaghi, F. Rizzo, J. Pedrini, A. Mauri, F. Meinardi, U. Cosentino, C. Greco, A. Moguzzi and A. Papagini, Photochem. Photobiol. Sci, 2022, 21, 913–921.
- 26 a) M. Goez, M. Schiewek and M. H. O. Musa, *Angew. Chem. Int. Ed.*, 2002, 41, 1535–1538; b) C. Creutz and N. Sutin, *Proc. Nat. Acad. Sci. USA*, 1975, 72, 2858–2862.
- 27 a) R. J. Crutchley, N. Kress and A. B. P. Lever, J. Am. Chem. Soc., 1983, 1170–1178; b) O. S. Wenger, Coord. Chem. Rev., 2015, 282-283, 150–158.
- 28 Y. Wei, Y. Li, Z. Li, X. Xu, X. Cao, X. Zhou and C. Yang, Inorg. Chem., 2021, 60, 19001–19008.
- 29 a) A. Juris and V. Balzani, *Coord. Chem. Rev.*, 1988, **84**, 85–277; b) C. T. Lin, W. Boettcher, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1976, **98**, 6536–6544.
- 30 a) N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, **116**, 10075–10166; b) D. P. Hari, T. Hering and B. König, *Org. Lett.*, 2012, **14**, 5334–5337.
- 31 T. Arai, T. Karatsu, H. Misawa, Y. Kuriyama, H. Okamoto, Hiresaki Tatsuro, H. Furuuchi, H. Zengm,
 H. Sakuragi and K. Tokumaru, *Pure & Appl. Chem.*, 1988, 7, 989–998.
- 32 F. Glaser and O. S. Wenger, Chem. Sci., 2022, 14, 149–161.
- 33 X.-J. Yang, B. Chen, L.-Q. Zheng, L.-Z. Wu and C.-H. Tung, *Green Chem.*, 2014, 16, 1082–1086.
- 34 V. Kasche and L. Lindquist, *Photochem. Photobiol.*, 1965, **4**, 923–933.
- 35 a) S. M. Hubig, J. Lumin., 1990, **47**, 137–145; b) C. Kerzig and M. Goez, *Phys. Chem. Chem. Phys.*, 2014, **16**, 25342–25349.