Table of Contents:

1. General section ........................................................................................................................................... S2

2. Experimental details..................................................................................................................................... S4
   2.1. Synthetic procedures.............................................................................................................................. S4
   2.2. $^{31}$P NMR shifts..................................................................................................................................... S8
   2.3. Selected crystallographic data ................................................................................................................. S8

3. Theoretical section......................................................................................................................................... S9

4. Electrochemical investigations of compounds 2, 3 and 4 ......................................................................... S13

5. Steady-state investigation of compounds 1-5............................................................................................... S14

6. NMR data ................................................................................................................................................... S15

7. Literature...................................................................................................................................................... S23
1. General section

Reactions were carried out in dry glassware and under inert atmosphere of purified argon or nitrogen using Schlenk techniques unless otherwise stated. Some solvents such as diethyl ether, dichloromethane, THF and toluene were used directly from a solvent purification system MB SPS-800. Pentane, MeOH and CHCl₃ were purchased from commercial suppliers and used as received. Dry pentane was prepared by adding molecular sieve to the commercial solvent. Aq. ammonia solution, tBuLi (1.7 M solution in pentane), P,P-dichlorophenylphosphine, methyl trifluoromethanesulfonate, elemental sulfur, trichlorosilane and tris(pentafluorophenyl)borane were purchased from commercial suppliers and used as received. Oxide 1a was synthesized according to our previous publication.[51]

NMR: ¹H, ¹¹B, ¹³C, ¹⁹F and ³¹P NMR as well as DEPT 135 spectra were recorded on a Bruker Avance III, Bruker Avance 400, Bruker Avance-III-300, Bruker Avance DRX-300, Bruker Avance 500 or Bruker Avance 600. Chemical shifts are expressed as parts per million (ppm, δ) and referenced to external 85% H₃PO₄ (³¹P), or solvent signals (¹H / ¹³C): Cl₂CDCl₃ (6.00 / 73.78 ppm), CDCl₃ (7.27 / 77.16 ppm), CD₂Cl₂ (5.33 / 53.80 ppm) and Acetone-d₆ (2.05 / 29.32 or 206.68) as internal standards. Signal descriptions include: s = singlet, d = doublet, t = triplet, m = multiplet and br = broad. All coupling constants are absolute values and J values are expressed in Hertz (Hz).

Mass spectrometry: MS and HRMS were measured at the Organisch-Chemisches Institut of the Heidelberg University. A Bruker ApexQe hybrid 9.4 T FT-ICR was used for DART, ESI and MALDI spectra, a JEOL JMS-700 magnetic sector for LIFDI spectra and a JEOL AccuTOF GCx time-of-flight for EI spectra.

X-Ray crystallography: X-ray crystal structure analysis was measured on a Stoe Stadivari instrument using Cu-Kα radiation. Diffraction intensities were corrected for Lorentz and polarization effects. An empirical scaling and absorption correction was applied using X-Area LANA 1.70.0.0 (STOE, 2017) based on the Laue symmetry of reciprocal space. The structure was solved with SHELXT-2014[52a] and refined against F² with the full-matrix least-squares algorithm using the SHELXL-2017/1 software.[52b] Hydrogen atoms were treated using appropriate riding models. The crystal structure of borane adduct 5 was obtained from a chlorobenzene solution by slow concentration at r.t. CCDC 1911633 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/.
Theoretical calculations: Molecular optimizations have been carried out at the B3LYP/6-31+G(d) level by using the GAUSSIAN 09 suite of programs.\textsuperscript{[S3]} Solvent effects (DCM) were considered by using the polarization continuum model (PCM).

Steady-state spectroscopy: Absorption and emission spectra were recorded using a Jasco V660 and Jasco FP6500 spectrometer, respectively.

Fluorescence quantum yields $\Phi$: Quantum yields were measured using quinine sulfate in 0.1M sulfuric acid as a reference ($\Phi = 0.54$) according to the literature.\textsuperscript{[S4]}

Fluorescence lifetimes $\tau$: The fluorescence decays were recorded with a HORIBA Scientific Fluorocube single photon counting system operated with HORIBA Scientific DataStation version 2.2. Fluorescence lifetimes were acquired by an exponential fit according to the least mean square with commercially available software HORIBA Scientific Decay Data Analyses 6 (DAS6) version 6.4.4.

Electrochemistry: Voltammograms (cyclic voltammetry, differential pulse voltammetry and square wave voltammetry) were recorded using a Metrohm Autolab PGSTAT101 potentiostat/galvanostat from acetonitrile solutions using tetrabutylammonium hexafluorophosphate as electrolyte, glassy carbon as working electrode, Pt wire as counter electrode and Ag wire as pseudo-reference electrode. Scan rate is 100 mV s$^{-1}$. The curves were calibrated using ferrocene as internal standard ($E_{1/2} = 0.54$ V vs SCE).
2. Experimental details

2.1. Synthetic procedures

**Diphosphahexaarene 2a and 2b**

In a flame-dried Schlenk flask with condenser, compound 1a (1.0 eq, 0.064 mmol, 40 mg) was suspended in 8 mL of degassed THF, trichlorosilane (30.0 eq, 1.921 mmol, 260 mg, 0.19 mL) was added and the mixture was stirred at 90 °C. After 19 h, 20 eq of HSiCl₃ were added at r.t. and the mixture was heated up again to 90 °C. This was repeated after 42 h and 48 h reaction time. After 68 h, $^{31}$P NMR analysis indicated complete conversion to a 1:1 mixture of isomers. The turbid solution was allowed to cool to r.t. and filtered through dry Celite®. After removing the solvent under vacuum at r.t. the product was washed with dry toluene, pentane and diethyl ether and finally purified by column chromatography under inert atmosphere using silica gel and DCM as eluent. The product was obtained in 40% yield as a mixture of two isomers.

$^1$H NMR (301 MHz, CD$_2$Cl$_2$): δ 8.76 (s, 2H), 8.55 (d, $J = 7.6$ Hz, 2H), 8.25 (d, $J = 12.9$ Hz, 2H), 7.98 – 7.89 (m, 6H), 7.70 (t, $J = 7.8$ Hz, 2H), 7.60 – 7.54 (m, 2H), 7.18 – 7.06 (m, 10H).

$^{13}$C{$^{1}$H}{$^{31}$P} and DEPT 135{$^{31}$P} NMR (151 MHz, DCM-d$_2$): δ 142.0 (C), 142.0 (C), 135.4 (C), 135.4 (CH), 135.3 (CH), 134.6 (C), 134.0 (CH), 134.0 (CH), 132.4 (C), 132.4 (C), 132.3 (C), 132.0 (CH), 132.0 (CH), 131.3 (C), 131.3 (C), 131.2 (C), 130.9 (C), 130.9 (C), 130.5 (CH), 130.5 (CH), 130.2 (CH), 128.7 (CH), 128.7 (CH), 128.6 (CH), 126.9 (CH), 126.1 (CH), 126.1 (CH), 126.1 (CH), 124.0 (CH), 124.0 (CH). $^{31}$P{$^{1}$H} NMR (122 MHz, DCM-d$_2$): δ -36.20, -36.46. HRMS (EI+) calcd. for [M]$^+$ C$_{42}$H$_{26}$P$_2$$^+$ 592.1504, found 592.1497.
In a flame-dried Schlenk flask, the tetrabromo starting material (1.0 eq, 0.137 mmol, 95 mg) was dissolved in a 1:1 mixture of THF (4.5 mL) and diethyl ether (4.5 mL). The solution was then cooled to -78 °C and ‘BuLi (4.0 eq, 0.546 mmol, 0.32 mL of a 1.7 M solution in pentane) was added dropwise. The solution was stirred at -78 °C for 30 min, covered from light, PhP<sub>Cl</sub> (2.1 eq, 0.287 mmol, 51 mg, 39 µL) was added and the solution was stirred at room temperature for 4.5 h. To the resulting suspension, elemental sulfur (2.5 eq, 0.341 mmol, 11 mg) was added and the mixture was stirred for 22 h at r.t. The solvent was removed under vacuum at r.t. The crude product was obtained in 80% conversion as a mixture of two isomers. Purification by column chromatography using silica gel and DCM/Pentane/MeOH/NH<sub>2</sub>OH 10:90:0.5:0.5 to 100:0:0.5:0.5 and then continuing with 100:0:2:1 to 100:0:4:1 as eluent mixtures allowed to isolate the two isomers. The pure products Isomer 1 (26% yield) and Isomer 2 (34% yield) were finally obtained as yellow solids by precipitation with methanol from chloroform solutions.

**Isomer 1:**<br>
\( ^1\text{H NMR} (600 \text{ MHz, CD}_2\text{Cl}_2): \delta 9.01 \text{ (d, } J = 17.1 \text{ Hz, } 2\text{H}), 8.84 \text{ (d, } J = 5.0 \text{ Hz, } 2\text{H}), 8.68 \text{ (d, } J = 7.4 \text{ Hz, } 2\text{H}), 8.56 \text{ (dd, } J = 17.1, 7.1 \text{ Hz, } 2\text{H}), 8.13 \text{ (br d, } J = 8.0 \text{ Hz, } 2\text{H}), 8.08 \text{ (br d, } J = 8.0 \text{ Hz, } 2\text{H}), 7.81 \text{ (t, } J = 7.8 \text{ Hz, } 2\text{H}), 7.72 – 7.69 \text{ (m, } 2\text{H}), 7.43 \text{ (dd, } J = 13.8, 7.4 \text{ Hz, } 4\text{H}), 7.27 – 7.25 \text{ (m, } 2\text{H}), 7.18 \text{ (td, } J = 7.7, 3.0 \text{ Hz, } 4\text{H}). \) \(^{13}\text{C}[^1\text{H}]\{[^3\text{P}] \text{ and DEPT 135 NMR (151 MHz, CD}_2\text{Cl}_2): \delta 137.4 \text{ (d, } J = 85.3 \text{ Hz, C}), 136.7 \text{ (s, C), 135.6 (d, } J = 4.2 \text{ Hz, C), 135.6 (d, } J = 10.4 \text{ Hz, CH), 133.9 (d, } J = 8.3 \text{ Hz, C), 133.8 (d, } J = 9.0 \text{ Hz, CH), 133.6 (d, } J = 2.8 \text{ Hz, CH), 131.3 (s, CH), 131.3 (s, CH), 131.1 (s, C), 130.3 (d, } J = 11.1 \text{ Hz, CH), 129.5 (d, } J = 7.6 \text{ Hz, C), 128.7 (d, } J = 12.5 \text{ Hz, CH), 128.4 (d, } J = 81.8 \text{ Hz, C), 127.4 (s, CH), 126.6 (d, } J = 14.6 \text{ Hz, CH), 126.2 (d, } J = 84.6 \text{ Hz, C), 126.1 (d, } J = 9.0 \text{ Hz, CH), 125.7 (s, CH). \) \(^{31}\text{P}[^1\text{H}] \text{ NMR (243 MHz, CD}_2\text{Cl}_2): \delta 21.76. \) \( \text{HRMS (MALDI+)} \text{ c.alcd. for [M+H]}^+ \text{ C}_{42}\text{H}_{27}\text{P}_2\text{S}_2^+ 657.1024, \) found 657.1007. \( \text{MS (EI+)} \text{ c.alcd. For [M]+ C}_{42}\text{H}_{26}\text{P}_2\text{S}_2^+ 656.1, \) found 656.1.

**Isomer 2:**<br>
\( ^1\text{H NMR} (600 \text{ MHz, CD}_2\text{Cl}_2): \delta 9.03 \text{ (d, } J = 17.3 \text{ Hz, } 2\text{H}), 8.84 \text{ (d, } J = 5.0 \text{ Hz, } 2\text{H}), 8.68 \text{ (d, } J = 7.2 \text{ Hz, } 2\text{H}), 8.56 \text{ (ddd, } J = 17.1, 7.0, 1.2 \text{ Hz, } 2\text{H}), 8.16 \text{ (d, } J = 8.3 \text{ Hz, } 2\text{H}), 8.07 \text{ (d, } J = 8.0 \text{ Hz, } 2\text{H}), 7.80 \text{ (t, } J = 7.8 \text{ Hz, } 2\text{H}), 7.77 – 7.74 \text{ (m, } 2\text{H}), 7.48 – 7.44 \text{ (m, } 4\text{H}), 7.32 – 7.29 \text{ (m, } 2\text{H}), 7.24 – 7.21 \text{ (m, } 4\text{H}). \) \(^{13}\text{C}[^1\text{H}]\{[^3\text{P}] \text{ and DEPT 135 NMR (151 MHz, CD}_2\text{Cl}_2): \delta \)
137.1 (C), 136.7 (C), 135.6 (CH), 135.6 (C), 133.9 (C), 133.8 (CH), 133.6 (CH), 131.4 (CH), 131.2 (CH), 130.5 (CH), 129.5 (C), 129.5 (C), 128.8 (CH), 128.7 (C), 127.4 (CH), 126.7 (CH), 126.2 (C), 126.1 (CH), 125.7 (CH). 

$^{31}$P$^{[1]}$H NMR (122 MHz, CDCl$_3$): $\delta$ 21.63. HRMS (MALDI+) calcd. for [M+H]$^+$ C$_{42}$H$_{27}$P$_2$S$_2$ $^+$ 657.1024, found 657.1073. MS (EI+) calcd. For [M]$^+$ C$_{42}$H$_{26}$P$_2$S$_2$ $^+$ 656.1, found 656.1.

**Diphosphahexaarene 4a and 4b**

In a flame-dried Schlenk flask with condenser, compound 1a (1.0 eq, 0.066 mmol, 41 mg) was suspended in 8 mL of THF, trichlorosilane (20.0 eq, 1.313 mmol, 178 mg, 0.13 mL) was added and the mixture was stirred at 90 °C. After 2 days, 20 eq of HSiCl$_3$ were added at r.t. and the mixture was heated up again. This was repeated after 4 days (20 eq) and 5 days (10 eq) reaction time. After 6 days reaction time, the cloudy solution was allowed to cool to r.t. and the volatiles were removed under vacuum at r.t. The yellow solid was dissolved in 11 mL of THF and cooled to 0 °C. Methyl trifluoromethanesulfonate (2.1 eq, 0.138 mmol, 23 mg, 16 μL) was added and the mixture was stirred at 0 °C. After 2h, the crude was filtered through a Celite plug and the solvent was removed under vacuum at r.t. The product was obtained in a 50% conversion as a mixture of two isomers. Purification by column chromatography using silica gel and CHCl$_3$/MeOH/NH$_4$OH 100:1:1 to 100:20:1 as eluent mixtures followed by precipitation from ethyl acetate solution with pentane/diethyl ether allowed to isolate the pure isomer mixture as yellow solid (Yield: 27%).

$^1$H NMR (301 MHz, Acetone-d$_6$): $\delta$ 9.67 (d, $J$ = 5.4 Hz, 2H), 9.50 (dd, $J$ = 16.5, 5.4 Hz, 2H), 9.18 (d, $J$ = 7.6 Hz, 2H), 8.70 – 8.60 (m, 4H), 8.46 (br d, $J$ = 8.1 Hz, 2H), 8.11 – 8.03 (m, 4H), 7.98 – 7.88 (m, 4H), 7.84 – 7.75 (m, 2H), 7.71 – 7.60 (m, 4H), 3.40 (d, $J$ = 14.4 Hz, 3H), 3.37 (d, $J$ = 14.4 Hz, 3H). $^{13}$C$^{[1]}$H$^{[31]}$P and DEPT 135 NMR (151 MHz, Acetone-d$_6$): $\delta$ 138.7 (C), 137.8 (CH), 137.7 (CH), 137.4 (CH), 137.4 (CH), 136.3 (C), 136.3 (C), 135.9 (CH), 135.9 (CH), 135.2 (CH), 135.1 (CH), 134.4 (C), 133.0 (CH), 133.0 (CH), 132.8 (CH), 132.8 (CH), 130.8 (C), 130.8 (C), 130.6 (CH), 130.6 (CH), 129.6 (C), 128.7 (CH), 128.7 (CH), 128.2 (CH), 128.2 (CH), 127.9 (CH), 127.8 (CH), 127.6 (C), 127.2 (CH), 124.4 (C), 124.4 (C), 122.9 (C), 120.8 (C), 115.8 (C), 115.7 (C), 111.6 (C), 111.5 (C), 10.2 (2xCH$_3$). $^{19}$F$^{[1]}$H NMR (283 MHz,
Acetone-d$_6$: $\delta$ -78.82. $^{31}$P{H} NMR (122 MHz, Acetone-d$_6$): $\delta$ 1.14, 1.10. HRMS (ESI$^+$) m/z calcd. for [M-OTf]$^+$ C$_{45}$H$_{32}$F$_3$O$_3$P$_2$S$^+$ 771.1494, found 771.1502; m/z calcd. for [M-2OTf]$^{2+}$ C$_{44}$H$_{32}$P$_2$$^+$ 311.0984, found 311.0984; m/z calcd. for [M-2OTf-H]$^+$ C$_{44}$H$_{31}$P$_2$$^+$ 621.1890, found 621.1895.

**Diphosphahexaarene 5**

![Diagram of Diphosphahexaarene 5]

In a flame-dried Schlenk tube, compound 1a (1.0 eq, 8.005 µmol, 5 mg) was dissolved in 3.8 mL of DCM. Tris(pentafluorophenyl)borane (2.05 eq, 16.410 µmol, 164 µL of 0.1 M solution in DCM) was added and the yellow solution stirred at r.t. for 70 min. The solvent was removed under vacuum and the crude was washed with dry pentane five times. After removal of the solvent under vacuum at 50 °C, the pure product was quantitatively isolated as a yellow solid.

$^1$H NMR (500 MHz, Cl$_2$CDCDCl$_2$): $\delta$ 8.97 (d, $J$ = 6.0 Hz, 2H), 8.76 (d, $J$ = 7.8 Hz, 2H), 8.31 – 8.27 (m, 4H), 8.16 (dd, $J$ = 8.0, 0.8 Hz, 2H), 8.06 (dd, $J$ = 15.8, 7.1 Hz, 2H), 7.89 (dt, $J$ = 17.2, 7.7 Hz, 6H), 7.69 – 7.63 (m, 4H), 7.59 – 7.55 (m, 4H). $^{13}$C{H} $^{31}$P and DEPT 135 NMR (151 MHz, Cl$_2$CDCDCl$_2$): $\delta$ 147.9 (C, BCF), 146.3 (C, BCF), 139.9 (C, BCF), 138.2 (C, BCF), 137.2 (CH), 137.2 (C, BCF), 137.0 (C), 136.8 (CH), 136.4 (C), 136.2 (CH), 135.5 (C), 135.5 (C, BCF), 133.9 (CH), 132.9 (C), 132.6 (CH), 132.2 (CH), 129.3 (CH), 129.0 (C), 129.0 (C), 127.5 (CH), 127.0 (C), 126.7 (CH), 126.0 (CH), 125.7 (C), 125.3 (CH), 120.9 (C), 118.8 (C, BCF), 117.1 (C), 99.4 (C). $^{19}$F{H} NMR (283 MHz, Cl$_2$CDCDCl$_2$) $\delta$ -132.2 (d, $J$ = 22.1 Hz, 6F), -158.04 (t, $J$ = 20.2 Hz, 3F), -163.97 – -164.11 (m, 6F). $^{31}$P{H} NMR (243 MHz, Cl$_2$CDCDCl$_2$) $\delta$ 23.02. MS (LIFDI): m/z calcd. for [M-BCF]$^+$ C$_{60}$H$_{26}$BF$_{13}$O$_2$P$_2$$^+$ 1136.1, found 1136.1.
2.2. \(^{31}\)P NMR shifts

**Table S1.** \(^{31}\)P NMR shifts of compounds 1-5, measured in CDCl\(_3\) solution. Chemical shifts are expressed as parts per million (ppm, \(\delta\)) and referenced to external 85% H\(_3\)PO\(_4\). In case of 2 and 4 the two isomers in the mixture exhibit different shifts, which are given separated by a slash.

| Oxide cis 1a | Ox. trans 1b | Reduced 2 | 3 Isomer 1 | 3 Isomer 2 | Quaternized 4 | BCF-Add. 5 |
|--------------|--------------|-----------|------------|------------|---------------|-------------|
| +8.30        | +9.06        | -34.63/-35.43 | +21.62     | +21.54     | -0.57/-0.61   | +22.17      |

2.3. Selected crystallographic data

**Table S2.** Selected crystallographic data of compound 5.

| Compound | 5 |
|----------|---|
| Empirical formula | C\(_{102}\)H\(_{46}\)B\(_2\)Cl\(_4\)F\(_30\)O\(_2\)P\(_2\) |
| Formula weight | 2098.75 |
| Temperature | 110(2) K |
| Wavelength | 1.54178 Å |
| Crystal system | monoclinic |
| Space group | P2\(_1\)/n |
| \(a\); \(\alpha\) | 21.8664(12) Å; \(\alpha = 90^\circ\) |
| \(b\); \(\beta\) | 13.7822(8) Å; \(\beta = 95.105(5)^\circ\) |
| \(c\); \(\gamma\) | 28.9308(18) Å; \(\gamma = 90^\circ\) |
| Volume | 8684.2(6) Å\(^3\) |
| Density (calculated) | 1.61 g/cm\(^3\) |
| Absorption coefficient | 2.65 mm\(^{-1}\) |
| Crystal shape | needle |
| Crystal size | 0.570 x 0.045 x 0.026 mm\(^3\) |
| Crystal colour | pale yellow |
| Theta range for data collection | 3.6 to 52.1\(^\circ\) |
| Index Ranges | -22\(<h\)<20, -7\(<k\)<13, -29\(<l\)<22 |
| Reflections collected | 18351 |
| Independent reflections | 9044 (R(int) = 0.0282) |
| Observed reflections | 6754 (I > 2\(\sigma(I)\)) |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.34 and 0.73 |
| Refinement method | Full-matrix least-squares on \(F^2\) |
| Data/restraints/parameters | 9044 / 1191 / 1279 |
| Goodness-of-fit on \(F^2\) | 1.07 |
| Final R indices (I>2\(\sigma(I)\)) | R1 = 0.054, wR2 = 0.134 |
| Largest diff. peak and hole | 1.52 and -0.60 eÅ\(^{-3}\) |
3. Theoretical section

Figure S1. Frontier molecular orbitals of compounds 2a, 2b, and 1a computed by DFT calculations.
Figure S2. Frontier molecular orbitals of compounds 3a, 3b, and 1a for comparison computed by DFT calculations.
Figure S3. Frontier molecular orbitals of compounds 4a, 4b, and 1a for comparison computed by DFT calculations.
Table S3. Orbital energy values in eV of compounds 1 to 4 computed by DFT calculations.

|        | 2a    | 2b    | 1a    | 3a    | 3b    | 4a    | 4b    |
|--------|-------|-------|-------|-------|-------|-------|-------|
| LUMO+2 | -1.536| -1.534| -1.885| -1.968| -1.980| -2.837| -2.835|
| LUMO+1 | -2.064| -2.052| -2.307| -2.345| -2.355| -3.208| -3.206|
| LUMO   | -2.097| -2.097| -2.369| -2.425| -2.408| -3.259| -3.257|
| HOMO   | -5.809| -5.806| -5.982| -6.053| -6.023| -6.815| -6.816|
| HOMO-1 | -5.840| -5.824| -6.256| -6.207| -6.198| -7.092| -7.090|
| HOMO-2 | -6.203| -6.198| -6.943| -6.363| -6.400| -7.87   | -7.871|
| HOMO-3 | -6.646| -6.681| -7.086| -6.501| -6.509| -7.964| -7.965|
| GAP    | 3.712 | 3.709 | 3.613 | 3.628 | 3.615 | 3.556 | 3.559 |

Figure S4. Most relevant molecular orbitals from compounds 1 to 4 computed by DFT calculations. See Table S3 for values
4. Electrochemical investigations of compounds 2, 3 and 4.

**Figure S5.** Voltammograms of 2, 3 and 4 obtained from acetonitrile solutions by cyclic voltammetry (top), differential pulse voltammetry (middle) and square wave voltammetry (bottom).

**Table S4.** Redox properties of compounds 1a,$^{1}$ 2, 3 and 4.

| Compound | Red.3 $E_{1/2}$ (V) | Red.2 $E_{1/2}$ (V) | Red.1 $E_{1/2}$ (V) | Ox.1 $E_{1/2}$ (V) |
|----------|---------------------|---------------------|---------------------|---------------------|
| 1a       |                     | -1.71               | -1.43               | 1.77                |
| 2        |                     | -1.87               | -1.63               | 1.01                |
| 3        |                     |                     | -1.44               | 1.35                |
| 4        | -1.6                | -1.26               | -1.1                |
5. Steady-state investigation of compounds 1-5

Table S5. Selected spectroscopic data from compounds 1-5

| Compound | Absorp. λ\textsubscript{max} (nm)<sup>a</sup> | Emission λ\textsubscript{max} (nm)<sup>b</sup> | Stokes shift (cm\textsuperscript{-1})<sup>d</sup> | τ (ns)<sup>e</sup> | Φ (%)<sup>f</sup> |
|----------|---------------------------------|-----------------|-----------------|---------|---------|
| 1a<sup>51</sup> | 343, 385, 405 | 415, 438, 463 | 595 | 6.2 | 84 |
| 2 | 354, 369(sh) | 415, 439, 465 | 4152 or 3004 (sh) | 6.9 | 10 |
| 3a,b | 347, 357(sh), 405 | 417, 440, 464(sh) | 711 | 5.8; 0.2 | 1 |
| 4 | 345(sh), 354, 392, 414 | 422, 447, 472(sh) | 458 | 6.8 | 80 |
| 4<sup>b</sup> | 348, 392, 412 | 423, 447 | 631 | 8.2; 4.3 | 67 |
| 5 | 348, 355, 402, 424 | 434, 460, 492(sh) | 543 | 5.1 | 78 |

[a] Absorption maxima recorded from DCM solutions unless specified. [b] Emission maxima recorded from aqueous solutions. [c] Emission maxima from DCM solutions unless specified. [d] The stokes shifts were calculated considering the absorption maxima with the lowest energy and emission maxima with the highest energy. The wavelengths were converted into the corresponding wavenumbers and then subtracted to obtain the Stokes shifts in cm\textsuperscript{-1}. [e] Fluorescence lifetimes. [f] Fluorescence quantum yields relative to quinine sulfate in 0.1 M H\textsubscript{2}SO\textsubscript{4}, Φ = 0.54. (sh) = shoulder.

Figure S6. Absorption (black) and emission (red) spectra of compound 4 in water.
6. NMR data

$^1$H NMR (301 MHz, CD$_2$Cl$_2$) of compound 2

$^{13}$C($^1$H){$^{31}$P} (151 MHz, CD$_2$Cl$_2$) of compound 2
$^{31}P\{^1H\}$ NMR (121 MHz, CD$_2$Cl$_2$) of compound 2

$^1$H NMR (600 MHz, CD$_2$Cl$_2$) of compound 3, isomer 1
$^{13}\text{C}^{[\text{H}]}^{[\text{P}]}$ (151 MHz, CD$_2$Cl$_2$) of compound 3, isomer 1

$^{31}\text{P}^{[\text{H}]}$ NMR (202 MHz, CD$_2$Cl$_2$) of compound 3, isomer 1
$^1$H NMR (600 MHz, CD$_2$Cl$_2$) of compound 3, isomer 2

$^{13}$C{$^1$H}{$^{31}$P} (151 MHz, CD$_2$Cl$_2$) of compound 3, isomer 2
$^{31}\text{P}$-$^{1}\text{H}$ NMR (122 MHz, CDCl$_3$) of compound 3, isomer 2

$^{1}\text{H}$ NMR (301 MHz, Acetone-$d_6$) of compound 4
$^{13}\text{C}^{[1\text{H}]^{[31\text{P}]}}$ (151 MHz, Acetone-$d_6$) of compound 4

$^{19}\text{F}^{[1\text{H}]}$ NMR (283 MHz, Acetone-$d_6$) of compound 4
$^{31}\text{P}^{1\text{H}}$ NMR (122 MHz, Acetone-d$_6$) of compound 4

$^{1}\text{H}$ NMR (500 MHz, CDCl$_3$) of compound 5
$^{13}$C($^1$H)($^{31}$P) (151 MHz, CDCl$_2$) of compound 5

$^{19}$F($^1$H) NMR (283 MHz, CDCl$_2$) of compound 5
$^{31}\text{P}^{1\text{H}}$ NMR (243 MHz, CD$_2$ClCD$_2$Cl) of compound 5

7. Literature

S1. P. Hindenberg, M. Busch, A. Paul, M. Bernhardt, P. Gemessy, F. Rominger, C. Romero-Nieto, *Angew. Chem. Int. Ed.* 2018, 57, 15157.

S2. a) "SHELXT" software for integrated space-group and crystal structure determination, Sheldrick G. M., *Acta Cryst.* 2015, A71, 3-8; b) "SHELXL-2017/1" software for structure refinement, Sheldrick G. M., *Acta Cryst.* 2015, C71, 3-8.

S3. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, 2009.

S4. W. H. Melhuish, *J. Phys. Chem.* 1961, 65, 229.