Supporting Information

for

Broadening the scope of uranyl photoreactivity: The oxidation of a uranyl complex anion in solid-state materials

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Table of Contents

Figure S1: Experimental PXRD pattern of Cs$_2$UO$_2$Cl$_4$. ................................................................. 3
Figure S2: Experimental PXRD pattern of ethyl-viologen diiodide. ......................................................... 4
Figure S3: Experimental PXRD pattern of propyl-viologen diiodide. ....................................................... 5
Figure S4: Experimental PXRD pattern of 1. ................................................................................................. 5
Figure S5: Experimental PXRD pattern of 2. ............................................................................................... 7
Figure S6: Experimental PXRD pattern of 3. ............................................................................................... 8
Figure S7: DFT ground state models for 1-3. ............................................................................................... 9
Table S1: Crystallographically determined bond lengths for 1. ................................................................. 10
Table S2: Crystallographically determined bond lengths for 2. .............................................................. 11
Table S3: Crystallographically determined bond lengths for 3. .............................................................. 12
Figure S8: Tauc plots of 1-3. ..................................................................................................................... 13
Figure S9: Luminescence study of 1-3 emission recovery. ...................................................................... 14
Figure S10: Plot of second order rate constant of 1-3 versus viologen reduction potential. ...... 15
Figure S11: Luminescence study of CsUO$_2$Cl$_4$ quenching and recovery. ......................................... 16
Figure S12: Kinetics of photoinduced emission quenching of Cs$_2$UO$_2$Cl$_4$. .................................... 17
Figure S13: Raman spectra of 1. ............................................................................................................... 18
Figure S14: Raman spectra of 2. ............................................................................................................... 19
Figure S15: Raman spectra of 3. ............................................................................................................... 20
Table S4: Rehm-Weller analysis of 1-3. .................................................................................................. 21
Table S5: Calculated changes in energy of 1-3 ....................................................................................... 22
Table S6: Bonding parameters of DFT ground state models for [UO$_2$Cl$_4$]$^2-$ ................................ 23
Table S7: Select bonding parameters (Å) of DFT ground state models for 1. ................................ 24
Table S8: Select bonding parameters (Å) of DFT ground state models for 2. ................................ 25
Table S9: TD-DFT calculated excited singlet states of 1 ................................................................. 26
Table S10: TD-DFT calculated electronic transitions for the *singlet* states of 1. ........................................ 27

Figure S16: Isodensity representations of TD-DFT calculated electronic transitions for the *singlet* states of 1 above 10% contribution. ......................................................... 28

Figure S17: Isodensity representations of TD-DFT calculated electronic transitions for the *singlet* states of 1 below 10% contribution. ......................................................... 29

Table S11: TD-DFT calculated electronic transitions for the degenerate *triplet* states of 1.…… 30

Figure S18: Isodensity representations of TD-DFT calculated electronic transitions for the *triplet* states of 1. .......................................................... 31

Table S12: TD-DFT calculated excited states of 2. ........................................................................ 32

Table S13: TD-DFT calculated electronic transitions of 2. .............................................................. 33

Figure S19: Isodensity representations of TD-DFT calculated electronic transitions for the *singlet* states of 2............................................................ 34

Table S14: TD-DFT calculated electronic transitions for the degenerate *triplet* states of 2…… 35

Figure S20: Isodensity representations of TD-DFT calculated electronic transitions for the *triplet* states of 2. .......................................................... 36

Table S15: TD-DFT calculated excited states of 3. ........................................................................ 37

Table S16: TD-DFT calculated electronic transitions for the *singlet* states of 3. ................. 38

Figure S21: Isodensity representations of TD-DFT calculated electronic transitions for the *singlet* states of 3............................................................ 39

Table S17: TD-DFT calculated electronic transitions for the *triplet* states of 3. ................. 41

Figure S22: Isodensity representations of TD-DFT calculated electronic transitions for the *triplet* states of 3. .......................................................... 42

Figure S23: Luminescence spectra of 1-3 in the absence of UV-light. ........................................ 43

Figure S24: Kinetics of photoinduced emission quenching of 1-3............................................. 44
Figure S1: Experimental PXRD pattern of Cs$_2$UO$_2$Cl$_4$ (blue) with overlayed peak positions calculated from ICSD entry #56859 crystallographic information file (red).
Figure S2: Experimental PXRD pattern of ethyl-viologen diiodide (blue) with overlayed peak positions calculated from CSD entry BEQKAJ01 crystallographic information file (red).
Figure S3: Experimental PXRD pattern of propyl-viologen diiodide (blue) with overlayed peak positions calculated from CSD entry ZIFTAM crystallographic information file (red).
Figure S4: Experimental PXRD pattern of 1 (blue) with overlayed peak positions calculated from crystallographic information file (red). Cesium chloride (green) is a coproduct of the synthesis and accounts for peaks not assigned to 1.
Figure S5: Experimental PXRD pattern of 2 (blue) with overlayed peak positions calculated from crystallographic information file (red). Cesium iodide (green) is a coproduct of the synthesis and accounts for peaks not assigned to 2.
Figure S6: Experimental PXRD pattern of 3 (blue) with overlayed peak positions calculated from crystallographic information file (red). Cesium iodide (green) is a coproduct of the
**Figure S7:** DFT ground state models for 1-3.

Model for 1

Model for 2

Model for 3
Table S1: Crystallographically determined bond lengths for 1.

| Atom 1 | Atom 2 | Bond Length (Å) | Atom 1 | Atom 2 | Bond Length (Å) |
|--------|--------|-----------------|--------|--------|-----------------|
| C1     | H1     | 0.95            | C6     | H6A    | 0.98            |
| C1     | C2     | 1.375(3)        | C6     | H6B    | 0.98            |
| C2     | H2     | 0.95            | C6     | H6C    | 0.98            |
| C2     | C3     | 1.397(4)        | N1     | C1     | 1.344(3)        |
| C3     | C4     | 1.394(3)        | N1     | C5     | 1.345(3)        |
| C3     | C3     | 1.490(3)        | N1     | C6     | 1.479(4)        |
| C4     | H4     | 0.95            | U1     | Cl1    | 2.6753          |
| C4     | C5     | 1.374(3)        | U1     | Cl2    | 2.6598          |
| C5     | H5     | 0.95            | U1     | O1     | 1.773           |
Table S2: Crystallographically determined bond lengths for 2.

| Atom 1 | Atom 2 | Bond Length (Å) | Atom 1 | Atom 2 | Bond Length (Å) |
|--------|--------|-----------------|--------|--------|-----------------|
| C1     | H1     | 0.95            | C6     | H6AB   | 0.99            |
| C1     | N1     | 1.344(3)        | C6     | C7     | 1.519(3)        |
| C1     | C2     | 1.375(4)        | C7     | H7A    | 0.98            |
| C2     | H2     | 0.95            | C7     | H7B    | 0.98            |
| C2     | C3     | 1.396(4)        | C7     | H7C    | 0.98            |
| C3     | C3     | 1.487(4)        | N1     | C5     | 1.352(3)        |
| C4     | H4     | 0.95            | N1     | C6     | 1.488(4)        |
| C4     | C3     | 1.401(3)        | U1     | Cl1    | 2.6666          |
| C5     | H5     | 0.95            | U1     | O1     | 1.767           |
| C5     | C4     | 1.375(4)        | U1     | Cl2    | 2.6837          |
| C6     | H6A    | 0.99            |        |        |                 |
Table S3: Crystallographically determined bond lengths for 3.

| Atom 1 | Atom 2 | Bond Length (Å) | Atom 1 | Atom 2 | Bond Length (Å) |
|--------|--------|-----------------|--------|--------|-----------------|
| C1     | C2     | 1.39(1)         | C7     | H7B    | 0.99            |
| C1     | C5     | 1.39(1)         | C7     | C8     | 1.53(1)         |
| C2     | H2     | 0.95            | C8     | H8A    | 0.98            |
| C2     | C3     | 1.39(1)         | C8     | H8B    | 0.98            |
| C3     | H3     | 0.95            | C8     | H8C    | 0.98            |
| C3     | N1     | 1.390(9)        | N1     | C4     | 1.390(9)        |
| C4     | H4     | 0.95            | N1     | C6     | 1.47(1)         |
| C4     | C5     | 1.39(1)         | U1     | Cl1    | 2.69(1)         |
| C5     | H5     | 0.95            | U1     | Cl2    | 2.68(1)         |
| C6     | H6A    | 0.99            | U1     | Cl3    | 2.694(3)        |
| C6     | H6B    | 0.99            | U1     | Cl4    | 2.621(3)        |
| C6     | C7     | 1.55(2)         | U1     | O1     | 1.72(1)         |
| C7     | H7A    | 0.99            | U1     | O2     | 1.78(1)         |
Figure S8: Tauc plots of 1-3 (red, green, and purple, respectively) used to describe the ground state singlet energy, used in the thermodynamic analysis (via the Rehm-Weller equation).
**Figure S9:** Luminescence spectra of the excitation and emission of samples of 1-3 at times 0 h (red) and 3 h (purple) of irradiation. This was followed by 20 h of darkness, whereby some of the quenching of emission was reversed (black). Average recovered emission intensity (difference in intensity after 3 hours of irradiation and after 20 hours of darkness) as a percentage of max intensity for 1-3 are 14.8%, 6.9%, and 20.7%, respectively.
Figure S10: Plot of second order rate constant of 1-3 versus viologen reduction potential.

\[ y = -0.14x - 0.02 \]

\[ R^2 = 1.00 \]
**Figure S11**: a) One of three luminescence studies of Cs$_2$UO$_2$Cl$_4$ composed of spectra taken at various times of irradiation with UV-light over the course of a 3-hour experiment. b) Luminescence spectra acquired of Cs$_2$UO$_2$Cl$_4$ at times 0 h (red) and 3 h (purple) of irradiation. This was followed by 20 h of darkness, whereby most of the quenching of emission was reversed (black). The average normalized max intensity of the recovered sample was calculated to be 107% of the intensity of emission at t=0. A value of >100% is attributed to spectra collection undergone before the t=0 scan to calibrate the instrument to the signal of the sample. The recovery occurs quickly enough in Cs$_2$UO$_2$Cl$_4$ that this phenomenon becomes evident in our emission recovery measurements.
Figure S12: Kinetics of photoinduced emission quenching of Cs$_2$UO$_2$Cl$_4$ plotted to a first order reaction rate law.
Figure S13: Raman spectra of 1 before (top) and after 2 hours of irradiation (bottom).
Figure S14: Raman spectra of 2 before (top) and after 2 hours of irradiation (bottom). Intensity of the bottom spectra is doubled to better display the spectral features.
Figure S15: Raman spectra of 3 before (top) and after 2 hours of irradiation (bottom).
Table S4: Rehm-Weller parameters of 1-3 and change in Gibbs free energy associated with the transfer of an electron from the [UO$_2$Cl$_4$]$^{2-}$ anion to the respective viologen cation.

| Reaction Pair          | $E_{ox}$ | $E_{red}$ | Absorption Edge ($E_s$) | $e_0^2/\varepsilon_\alpha$ | $\Delta G$  |
|------------------------|----------|-----------|-------------------------|-----------------------------|-------------|
| [UO$_2$Cl$_4$]$^{2-}$/MV$^{2+}$ | -1.358 V | -0.446 V  | 2.445 eV                | 0.15 V                      | -3.507 eV   |
| [UO$_2$Cl$_4$]$^{2-}$/EV$^{2+}$ | -1.358 V | -0.449 V  | 2.178 eV                | 0.15 V                      | -3.237 eV   |
| [UO$_2$Cl$_4$]$^{2-}$/PV$^{2+}$ | -1.358 V | -0.635 V  | 2.092 eV                | 0.15 V                      | -2.965 eV   |
Table S5: Calculated changes in energy (\(\Delta E / \text{kJ/mol}\)) of \([\text{UO}_2\text{Cl}_4]^{n-}\) and viologen units found in 1-3. Singlet ground state energies of \([\text{UO}_2\text{Cl}_4]^{2-}\) and RV\(^{2+}\) used as reference values.

| Species         | Spin  | \(\Delta E\) |
|-----------------|-------|---------------|
| \([\text{UO}_2\text{Cl}_4]^{2-}\) | Singlet | 0 kJ/mol      |
| \([\text{UO}_2\text{Cl}_4]^{-}\)  | Doublet | +180 kJ/mol   |
| \([\text{UO}_2\text{Cl}_4]^{2-}\) | Triplet | +221 kJ/mol   |
| \([\text{UO}_2\text{Cl}_4]^{3-}\) | Doublet | +502 kJ/mol   |
| \(\text{MV}^{2+}\)   | Singlet | 0 kJ/mol      |
| \(\text{MV}^{+}\)    | Triplet | -869 kJ/mol   |
| \(\text{MV}^{3+}\)   | Triplet | +1645 kJ/mol  |
| \(\text{EV}^{2+}\)   | Singlet | 0 kJ/mol      |
| \(\text{EV}^{+}\)    | Triplet | -852 kJ/mol   |
| \(\text{EV}^{3+}\)   | Triplet | +1608 kJ/mol  |
| \(\text{PV}^{2+}\)   | Singlet | 0 kJ/mol      |
| \(\text{PV}^{+}\)    | Triplet | -856 kJ/mol   |
| \(\text{PV}^{3+}\)   | Triplet | +1523 kJ/mol  |
**Table S6:** Bonding parameters of DFT ground state models for [UO$_2$Cl$_4$]$^{2-}$.

| Charge Spin | 2- Singlet | 2- Triplet | 1- Doublet | 3- Triplet |
|-------------|-------------|------------|------------|------------|
| U-O         | 1.7738 Å    | 1.8221 Å   | 1.7664 Å   | 1.8198 Å   |
| U-Cl        | 2.7464 Å    | 2.7622 Å   | 2.6763 Å   | 3.0208 Å   |
**Table S7:** Select bonding parameters (Å) of DFT ground state models for 1.

| Atom1 | Atom2 | Calc Length | Exp Length | Calc Length | Exp Length |
|-------|-------|-------------|------------|-------------|------------|
| U     | Cl    | 2.7439      | 2.6748     | C           | 1.4339     |
| U     | Cl    | 2.7531      | 2.6587     | C           | 1.3779     |
| U     | Cl    | 2.7439      | 2.675      | C           | 1.3752     |
| U     | Cl    | 2.7531      | 2.6602     | C           | 1.4456     |
| U     | O     | 1.7927      | 1.7735     | C           | 1.4402     |
| U     | O     | 1.7926      | 1.7721     | C           | 1.4394     |
| N     | C     | 1.3761      | 1.3429     | C           | 1.3768     |
| N     | C     | 1.3787      | 1.3456     | C           | 1.3747     |
| N     | C     | 1.4791      | 1.4786     | C           | 1.4404     |
| N     | C     | 1.387       | 1.3438     | C           | 1.4392     |
| N     | C     | 1.3844      | 1.3448     | C           | 1.3762     |
| N     | C     | 1.4782      | 1.4786     | C           | 1.3789     |
| N     | C     | 1.3878      | 1.3429     | C           | 1.446      |
| N     | C     | 1.3852      | 1.3448     | C           | 1.4352     |
| N     | C     | 1.4772      | 1.4792     | C           | 1.4338     |
| N     | C     | 1.3748      | 1.3444     | C           | 1.3777     |
| N     | C     | 1.379       | 1.345      | C           | 1.3709     |
| N     | C     | 1.4802      | 1.4792     | C           | 1.4471     |
| N     | C     | 1.389       | 1.3444     | C           | 1.4468     |
| N     | C     | 1.3887      | 1.345      | C           | 1.3724     |
| N     | C     | 1.4725      | 1.4785     | C           | 1.3715     |
| N     | C     | 1.3895      | 1.3442     | C           | 1.4304     |
| N     | C     | 1.3874      | 1.345      | C           | 1.446      |
| N     | C     | 1.4741      | 1.4779     | C           | 1.4473     |
| N     | C     | 1.3895      | 1.3433     | C           | 1.3724     |
| N     | C     | 1.3875      | 1.3459     | C           | 1.3709     |
| N     | C     | 1.4741      | 1.4779     | C           | 1.447      |
| N     | C     | 1.389       | 1.3442     | C           | 1.4465     |
| N     | C     | 1.3887      | 1.345      | C           | 1.3717     |
| N     | C     | 1.4733      | 1.4779     | C           | 1.3709     |
| C     | C     | 1.3784      | 1.3758     | C           | 1.431      |
| C     | C     | 1.4349      | 1.3965     | C           | 1.4469     |
| C     | C     | 1.3717      | 1.3747     | C           | 1.4468     |
Table S8: Select bonding parameters (Å) of DFT ground state models for 2.

| Atom 1 | Atom 2 | Lengt h | Lengt h | Atom 1 | Atom 2 | Lengt h | Lengt h | Atom 1 | Atom 2 | Lengt h | Lengt h |
|--------|--------|---------|---------|--------|--------|---------|---------|--------|--------|---------|---------|
| U      | Cl     | 2.7157  | 2.669   | C      | C      | 1.3798  | 1.3784  | C      | C      | 1.4014  | 1.3997  |
| U      | Cl     | 2.7155  | 2.686   | C      | C      | 1.5252  | 1.5218  | C      | C      | 1.3837  | 1.3784  |
| U      | Cl     | 2.7155  | 2.669   | C      | C      | 1.3779  | 1.3767  | C      | C      | 1.5228  | 1.5224  |
| U      | Cl     | 2.7138  | 2.6843  | C      | C      | 1.4846  | 1.4925  | C      | C      | 1.3779  | 1.3769  |
| U      | O      | 1.7752  | 1.7697  | C      | C      | 1.401   | 1.4004  | C      | C      | 1.4019  | 1.4007  |
| U      | O      | 1.7753  | 1.7697  | C      | C      | 1.4025  | 1.3997  | C      | C      | 1.403   | 1.4008  |
| N      | C      | 1.3521  | 1.3426  | C      | C      | 1.3808  | 1.3787  | C      | C      | 1.38    | 1.3776  |
| N      | C      | 1.3456  | 1.3521  | C      | C      | 1.5216  | 1.5218  | C      | C      | 1.5219  | 1.5216  |
| N      | C      | 1.5038  | 1.4928  | C      | C      | 1.3804  | 1.3763  | C      | C      | 1.3798  | 1.378   |
| N      | C      | 1.3514  | 1.3431  | C      | C      | 1.4024  | 1.4007  | C      | C      | 1.4838  | 1.4912  |
| N      | C      | 1.3512  | 1.3523  | C      | C      | 1.4014  | 1.3997  | N      | C      | 1.3502  | 1.3523  |
| N      | C      | 1.5024  | 1.4916  | C      | C      | 1.3842  | 1.3784  | N      | C      | 1.5031  | 1.4924  |
| N      | C      | 1.3541  | 1.3426  | C      | C      | 1.5228  | 1.521   | N      | C      | 1.3526  | 1.3426  |
| N      | C      | 1.3477  | 1.3523  | C      | C      | 1.3818  | 1.3767  | N      | C      | 1.3449  | 1.3523  |
| N      | C      | 1.5036  | 1.4928  | C      | C      | 1.486   | 1.4918  | N      | C      | 1.5042  | 1.4924  |
| N      | C      | 1.3479  | 1.3426  | C      | C      | 1.4013  | 1.4007  | C      | C      | 1.3805  | 1.3763  |
| N      | C      | 1.3491  | 1.3523  | C      | C      | 1.4001  | 1.3997  | C      | C      | 1.402   | 1.4004  |
| N      | C      | 1.5148  | 1.4924  | C      | C      | 1.3822  | 1.3787  | C      | C      | 1.4002  | 1.3997  |
| N      | C      | 1.3477  | 1.3426  | C      | C      | 1.5251  | 1.521   | C      | C      | 1.4026  | 1.4004  |
| N      | C      | 1.3475  | 1.3521  | C      | C      | 1.3818  | 1.3769  | C      | C      | 1.3997  | 1.3997  |
| N      | C      | 1.5152  | 1.4924  | C      | C      | 1.4008  | 1.4004  | C      | C      | 1.3794  | 1.3784  |
| N      | C      | 1.3531  | 1.3426  | C      | C      | 1.4014  | 1.4003  | C      | C      | 1.5261  | 1.5216  |
| N      | C      | 1.3487  | 1.3521  | C      | C      | 1.3828  | 1.3784  | C      | C      | 1.3804  | 1.3772  |
| N      | C      | 1.5043  | 1.4924  | C      | C      | 1.5251  | 1.5224  | N      | C      | 1.352   | 1.3426  |
| C      | C      | 1.4864  | 1.492   | C      | C      | 1.4024  | 1.4004  |
Table S9: TD-DFT calculated excited *singlet* states of 1 between 330 nm and 370 nm.

| State no. | Wavelength | f-oscillation |
|-----------|------------|---------------|
| State 82  | 330.18 nm  | 0.0000        |
| State 81  | 330.90 nm  | 0.0000        |
| State 80  | 331.85 nm  | 0.0001        |
| State 79  | 331.86 nm  | 0.0000        |
| State 78  | 332.17 nm  | 0.0000        |
| State 77  | 332.81 nm  | 0.0000        |
| State 76  | 333.34 nm  | 0.0000        |
| State 75  | 334.18 nm  | 0.0026        |
| State 74  | 334.19 nm  | 0.0003        |
| State 73  | 336.01 nm  | 0.0000        |
| State 72  | 336.19 nm  | 0.0000        |
| State 71  | 344.91 nm  | 0.0000        |
| State 70  | 346.27 nm  | 0.0000        |
| State 69  | 347.35 nm  | 0.0000        |
| State 68  | 350.08 nm  | 0.0000        |
| State 67  | 352.07 nm  | 0.0000        |
| State 66  | 352.09 nm  | 0.0008        |
| State 65  | 352.17 nm  | 0.0000        |
| State 64  | 353.44 nm  | 0.0000        |
| State 63  | 355.09 nm  | 0.0000        |
| State 62  | 356.97 nm  | 0.0000        |
| State 61  | 358.50 nm  | 0.0187        |
| State 60  | 358.61 nm  | 0.0000        |
| State 59  | 359.32 nm  | 0.0000        |
| State 58  | 359.44 nm  | 0.0050        |
| State 57  | 359.79 nm  | 0.0000        |
| State 56  | 360.74 nm  | 0.0237        |
| State 55  | 361.40 nm  | 0.0000        |
| State 54  | 365.79 nm  | 0.0002        |
| State 53  | 366.16 nm  | 0.0002        |
| State 52  | 368.42 nm  | 0.0001        |
| State 51  | 369.01 nm  | 0.0004        |
| State 50  | 371.75 nm  | 0.0067        |
| State 49  | 372.12 nm  | 0.0000        |
| State 48  | 374.19 nm  | 0.0000        |
| State 47  | 376.67 nm  | 0.0001        |
Table S10: TD-DFT calculated electronic transitions for the *singlet* state of 1 at 358.50 nm

| Donor            | Acceptor       | Coefficient | Percent Contribution |
|------------------|----------------|-------------|----------------------|
| 253 (HOMO-2)     | 261 (LUMO+5)  | 0.46400     | 46%                  |
| 253 (HOMO-2)     | 263 (LUMO+7)  | -0.30754    | 20%                  |
| 245 (HOMO-10)    | 257 (LUMO+1)  | -0.26576    | 15%                  |
| 254 (HOMO-1)     | 263 (LUMO+7)  | -0.20705    | 9%                   |
| 253 (HOMO-2)     | 262 (LUMO+6)  | 0.13137     | 4%                   |
| 255 (HOMO)       | 262 (LUMO+6)  | 0.10841     | 3%                   |
| 255 (HOMO)       | 263 (LUMO+7)  | 0.12537     | 3%                   |
Figure S16: Isodensity representations of TD-DFT calculated electronic transitions for the *singlet* state of 1 at 358.50 nm with a percent contribution >10%.
Figure S17: Isodensity representations of TD-DFT calculated electronic transitions for the singlet state of 1 at 358.50 nm with a percent contribution <10%.
Table S11: TD-DFT calculated electronic transitions for the degenerate triplet states of 1 at 438 nm.

| Energy     | Donor          | Acceptor       | Coefficient | Percent Contribution |
|------------|----------------|----------------|-------------|----------------------|
| 437.87 nm  | 249 (HOMO-6)   | 258 (LUMO+2)   | 0.67808     | 100%                 |
| 437.52 nm  | 249 (HOMO-6)   | 259 (LUMO+3)   | 0.67819     | 100%                 |
Figure S18: Isodensity representations of TD-DFT calculated electronic transitions for the degenerate *triplet* states of 1 at 437.87 (Top) and 437.52 nm (Bottom).
Table S12: TD-DFT calculated excited states of 2 between 330 nm and 370 nm.

| State no. | Wavelength | f-oscillation |
|-----------|------------|---------------|
| State 60  | 333.49 nm  | 0.0000        |
| State 59  | 334.18 nm  | 0.0223        |
| State 58  | 335.22 nm  | 0.0000        |
| State 57  | 335.89 nm  | 0.0084        |
| State 56  | 337.15 nm  | 0.0000        |
| State 55  | 337.39 nm  | 0.0005        |
| State 54  | 339.01 nm  | 0.0000        |
| State 53  | 339.20 nm  | 0.0000        |
| State 52  | 341.41 nm  | 0.0228        |
| State 51  | 343.64 nm  | 0.0011        |
| State 50  | 344.08 nm  | 0.0000        |
| State 49  | 345.85 nm  | 0.0003        |
| State 48  | 347.19 nm  | 0.0000        |
| State 47  | 348.74 nm  | 0.0000        |
| State 46  | 348.88 nm  | 0.0001        |
| State 45  | 355.51 nm  | 0.0013        |
| State 44  | 355.66 nm  | 0.0000        |
| State 43  | 356.67 nm  | 0.0002        |
| State 42  | 356.82 nm  | 0.0000        |
| State 41  | 357.66 nm  | 0.0062        |
| State 40  | 357.85 nm  | 0.0037        |
| State 39  | 360.20 nm  | 0.0047        |
| State 38  | 362.01 nm  | 0.0000        |
| State 37  | 362.73 nm  | 0.0007        |
| State 36  | 363.20 nm  | 0.0000        |
| State 35  | 364.10 nm  | 0.0057        |
| State 34  | 364.16 nm  | 0.0000        |
| State 33  | 364.17 nm  | 0.0032        |
| State 32  | 364.72 nm  | 0.0000        |
| State 31  | 367.57 nm  | 0.0007        |
| State 30  | 367.69 nm  | 0.0000        |
| State 29  | 369.73 nm  | 0.0000        |
Table S13: TD-DFT calculated electronic transitions for the singlet state of 2 at 341.41 nm.

| Donor        | Acceptor       | Coefficient | Percent Contribution |
|--------------|----------------|-------------|----------------------|
| 286 (HOMO-1) | 293 (LUMO+5)   | 0.59734     | 76%                  |
| 286 (HOMO-1) | 295 (LUMO+7)   | -0.21157    | 10%                  |
| 287 (HOMO)   | 295 (LUMO+7)   | 0.19477     | 8%                   |
| 287 (HOMO)   | 294 (LUMO+6)   | 0.14023     | 4%                   |
| 286 (HOMO-1) | 294 (LUMO+6)   | -0.10899    | 3%                   |
**Figure S19:** Isodensity representations of TD-DFT calculated electronic transitions for the *singlet* state of 2 at 341.41 nm.
Table S14: TD-DFT calculated electronic transitions for the degenerate *triplet* states of 2 at 434 nm.

| Energy       | Donor            | Acceptor        | Coefficient | Percent Contribution |
|--------------|------------------|-----------------|-------------|----------------------|
| 434.41 nm    | 287 (HOMO) → 288 (LUMO) | 0.68004         | 94%         |
|              | 287 (HOMO) → 291 (LUMO+3) | -0.11993        | 3%          |
|              | 283 (HOMO-4) → 289 (LUMO+1) | 0.12803        | 3%          |
| 434.30 nm    | 287 (HOMO) → 291 (LUMO+1) | 0.68672         | 97%         |
|              | 283 (HOMO-4) → 288 (LUMO) | 0.12779         | 3%          |
Figure S20: Isodensity representations of TD-DFT calculated electronic transitions for the degenerate *triplet* states of 2 at 434.41 (Top) and 434.30 nm (Bottom).
Table S15: TD-DFT calculated excited states of 3 between 320 nm and 345 nm.

| State no. | Wavelength  | f-oscillation |
|-----------|-------------|---------------|
| State 83  | 320.08 nm   | 0.0018        |
| State 82  | 320.25 nm   | 0.0047        |
| State 81  | 320.71 nm   | 0.0044        |
| State 80  | 321.82 nm   | 0.0059        |
| State 79  | 322.18 nm   | 0.0057        |
| State 78  | 322.36 nm   | 0.0046        |
| State 77  | 322.77 nm   | 0.2048        |
| State 76  | 322.86 nm   | 0.0081        |
| State 75  | 323.21 nm   | 0.0645        |
| State 74  | 323.65 nm   | 0.0004        |
| State 73  | 323.78 nm   | 0.0818        |
| State 72  | 324.05 nm   | 0.1101        |
| State 71  | 324.19 nm   | 0.0130        |
| State 70  | 324.29 nm   | 0.0051        |
| State 69  | 325.04 nm   | 0.0464        |
| State 68  | 325.13 nm   | 0.4359        |
| State 67  | 326.35 nm   | 0.0023        |
| State 66  | 326.38 nm   | 0.0008        |
| State 65  | 326.45 nm   | 0.0324        |
| State 64  | 327.78 nm   | 0.0000        |
| State 63  | 328.05 nm   | 0.0112        |
| State 62  | 328.1 nm    | 0.0429        |
| State 61  | 328.18 nm   | 0.0078        |
| State 60  | 329.56 nm   | 0.0567        |
| State 59  | 331.07 nm   | 0.0672        |
| State 58  | 333.19 nm   | 0.0448        |
| State 57  | 333.71 nm   | 0.0016        |
| State 56  | 334.39 nm   | 0.0449        |
| State 55  | 340.52 nm   | 0.0114        |
| State 54  | 340.95 nm   | 0.0000        |
| State 53  | 341.03 nm   | 0.0005        |
| State 52  | 342.47 nm   | 0.0005        |
| State 51  | 344.14 nm   | 0.0219        |
Table S16: TD-DFT calculated electronic transitions for the *singlet* state of 3 at 325.13 nm.

| Donor (HOMO-n) | Acceptor (LUMO) | Coefficient | Percent Contribution |
|---------------|-----------------|-------------|----------------------|
| 304 (HOMO-15) | 320 (LUMO)      | 0.38175     | 34%                  |
| 305 (HOMO-14) | 320 (LUMO)      | 0.32682     | 25%                  |
| 299 (HOMO-20) | 320 (LUMO)      | -0.31502    | 23%                  |
| 306 (HOMO-13) | 320 (LUMO)      | -0.16638    | 7%                   |
| 306 (HOMO-13) | 322 (LUMO+2)    | -0.14403    | 5%                   |
| 316 (HOMO-3)  | 327 (LUMO+7)    | 0.11240     | 3%                   |
| 315 (HOMO-2)  | 325 (LUMO+5)    | 0.10889     | 3%                   |
Figure S21: Isodensity representations of TD-DFT calculated electronic transitions for the *singlet* state of 3 at 325.13 nm.
Table S17: TD-DFT calculated electronic transitions for the triplet states of 3 at 440 nm.

| Energy   | Donor       | Acceptor   | Coefficient | Percent Contribution |
|----------|-------------|------------|-------------|----------------------|
| 439.76 nm| 311 (HOMO-8)→ 320 (LUMO) | 0.10699    | 81%         |
|          | 312 (HOMO-7)→ 320 (LUMO) | 0.61575    | 17%         |
|          | 304 (HOMO-15)→ 320 (LUMO) | 0.27868    | 2%          |
**Figure S22:** Isodensity representations of TD-DFT calculated electronic transitions for the *triplet* states of 3 at 440 nm.
Figure S23: Kinetic spectra showing lack of quenching of samples 1-3 in the absence of UV-light irradiation. Spectra taken before (red) and after (purple) three hour periods.
Figure S24: Kinetics of photoinduced emission quenching of 1-3 plotted to a first order reaction rate law.