Electronic Supplementary Material (ESI) for Dalton Transactions

Yellow-light sensitization of a ligand photosubstitution reaction in a ruthenium polypyridyl complex covalently bound to a rhodamine dye

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Supporting Information

^{1}H NMR Spectra of the synthesized compounds

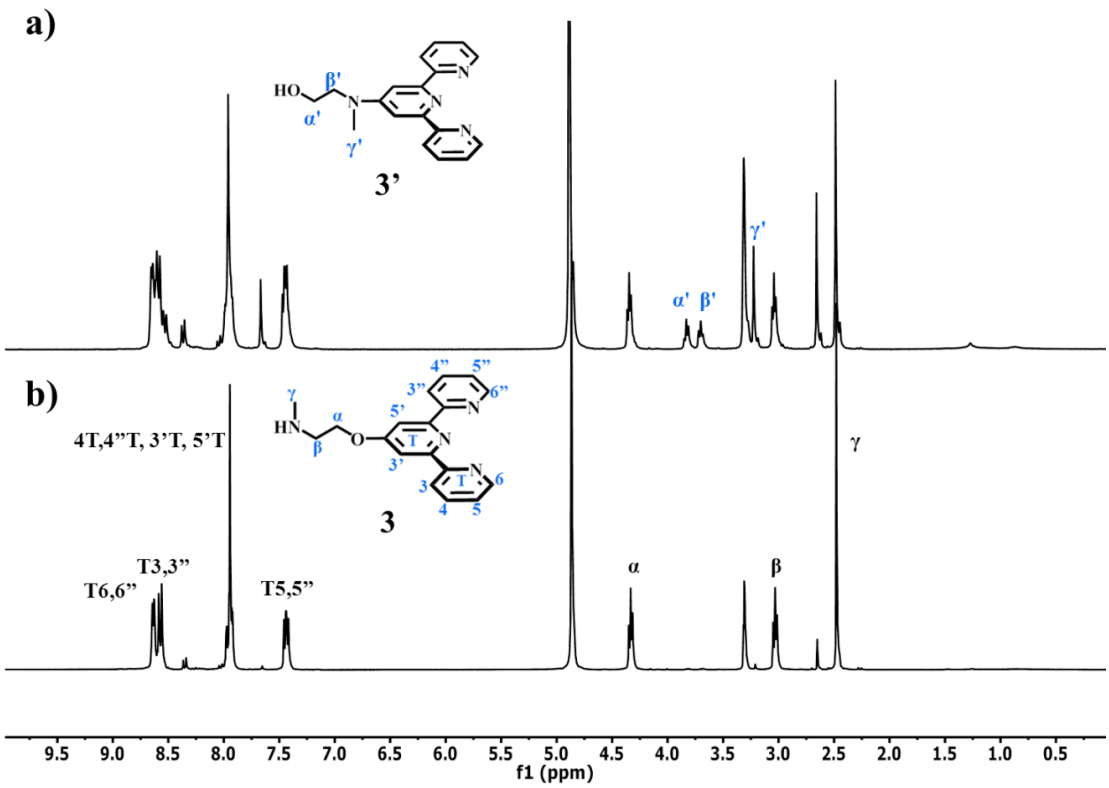

Figure S1. ^{1}H NMR spectra of a mixture of compounds **3** and **3'** (a), and of pure compound **3** (b) in methanol-d4. Atom numbering is given for proton attribution. Reaction conditions: a) 5 eq. KOH, DMSO (dry), heating at 60 °C, 36 h. b) 2.8 eq KOH, DMSO (dry), heating at 60 °C for 3 h, overnight at r.t.

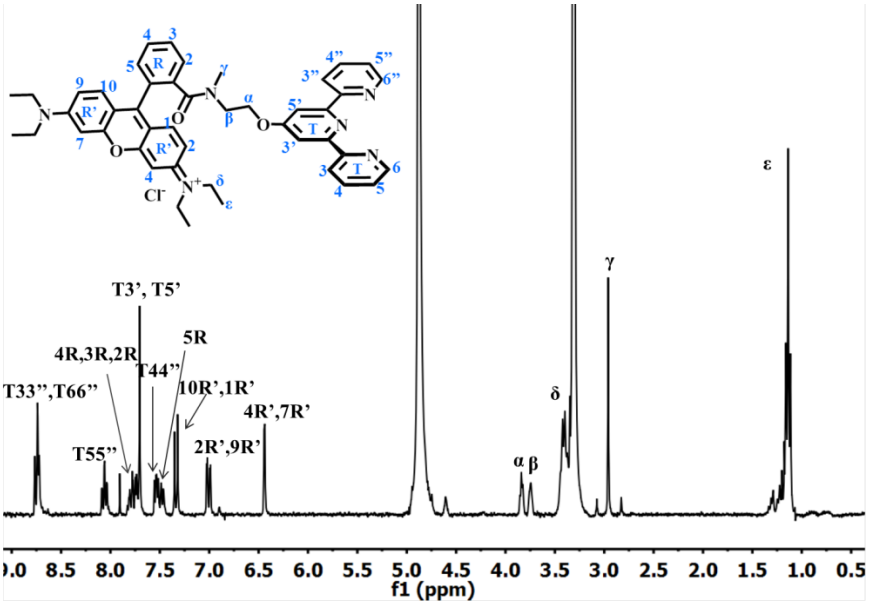

Figure S2. ^{1}H NMR spectrum of compound [**4**]Cl in methanol-d4 and atom numbering for proton attribution.

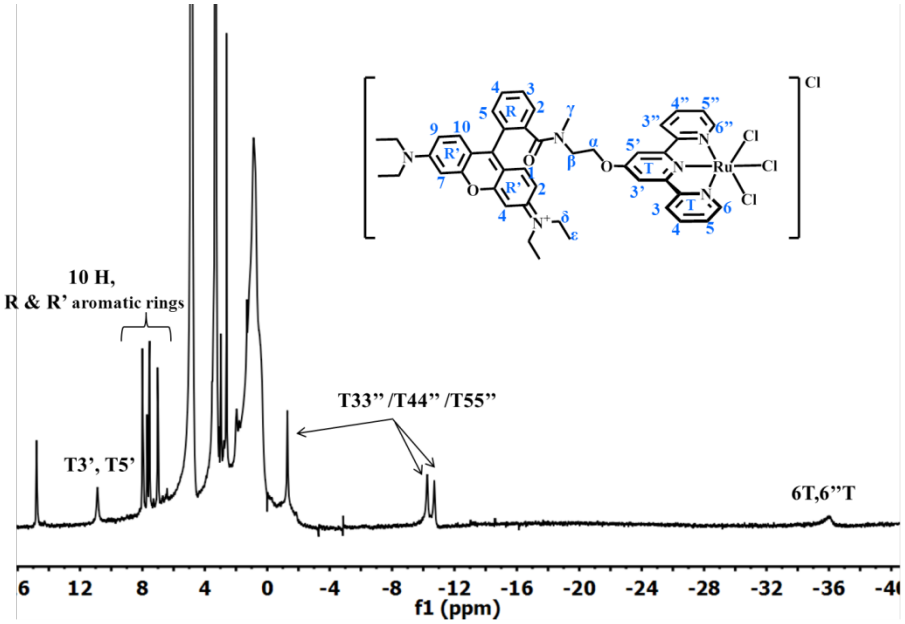

Figure S3. Paramagnetic ^{1}H NMR spectrum of compound **[5]**Cl in methanol-d4 and atom numbering for proton attribution.

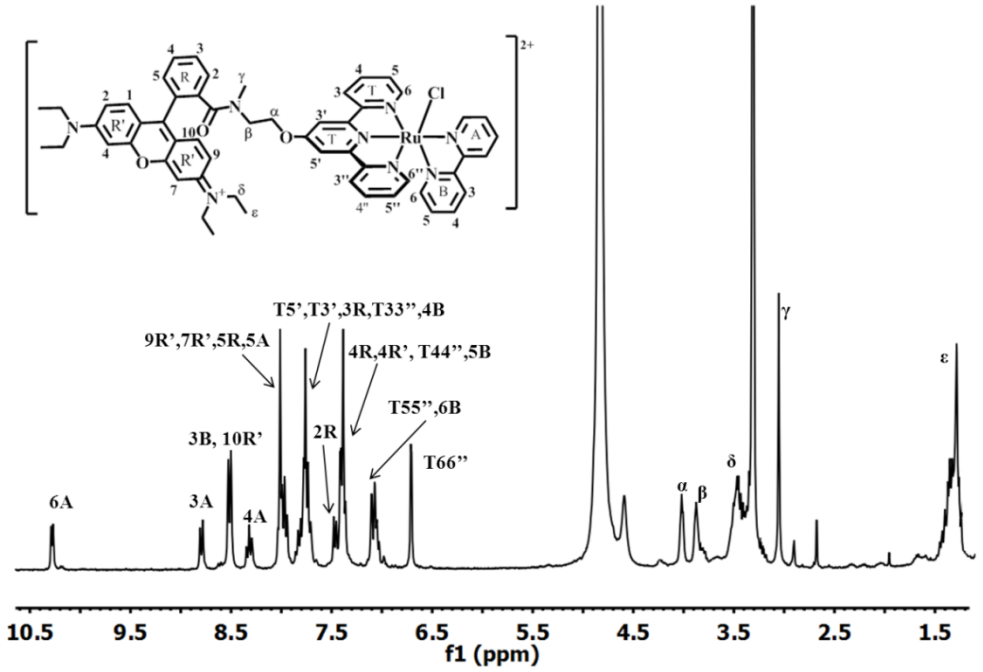

Figure S4. ^{1}H NMR spectrum of compound [**6**](PF$_6$)$_2$ in methanol-d4 and atom numbering for proton attribution.

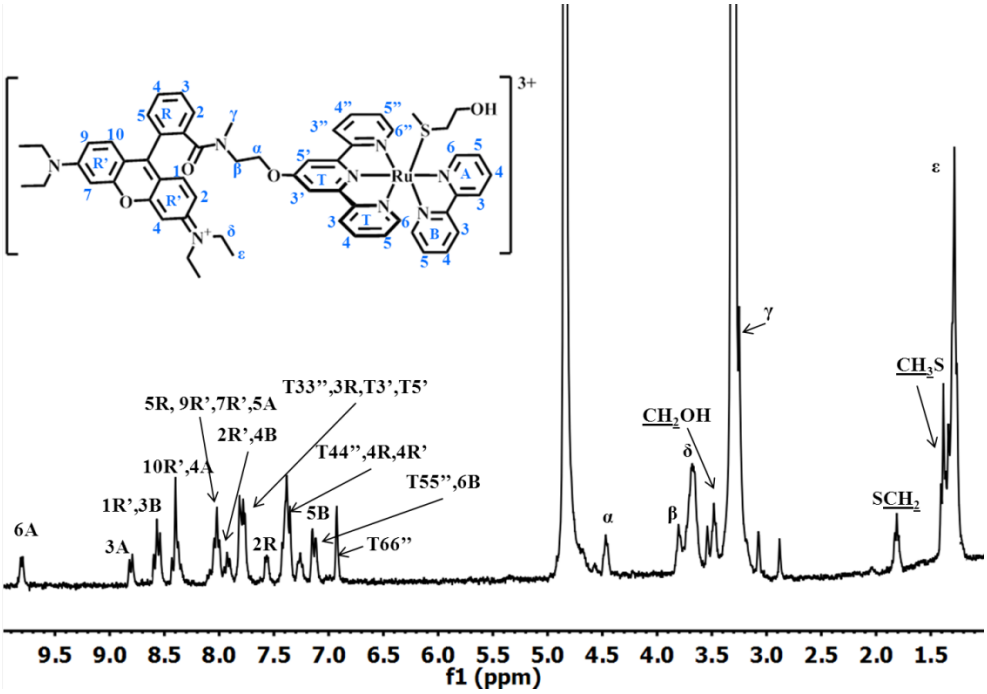

Figure S5. ^{1}H NMR spectrum of compound [**2**]Cl$_3$ in methanol-d4 and atom numbering for proton attribution.

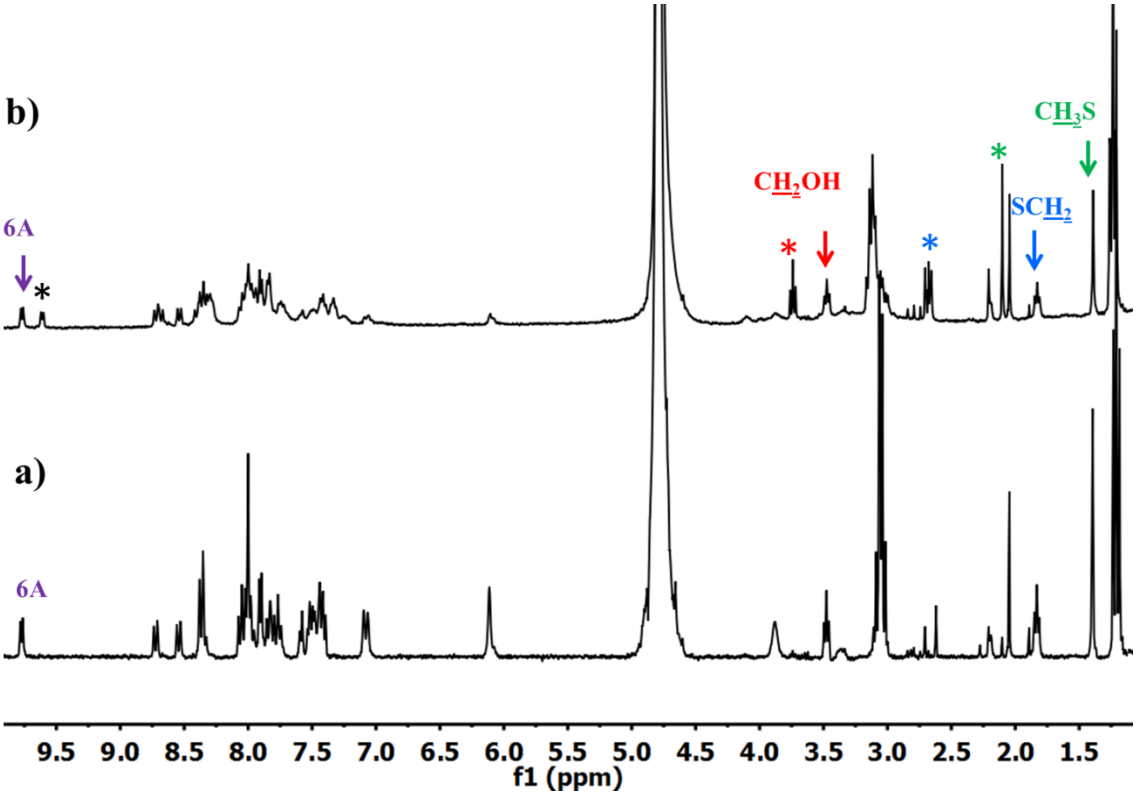

Figure S6. ^{1}H NMR spectra of [**2**]Cl_3 in (region 10–1.0 ppm) in D_2O before (a) and after (b) irradiation with yellow light for 530 min. The arrows show the peaks of coordinated Hmte and 6A in $[\mathbf{2}]^{3+}$, and the stars indicate free Hmte (aliphatic part) and 6A in $[Ru(\mathbf{4})(bpy)(D_2O)]^{3+}$ (aromatic part). Conditions: Yellow light irradiation (λ_e=570 nm, $\Delta\lambda_{1/2}$=8.9 nm, t=530 min), photon flux: 5.3×10^{-9}, $[Ru]_{tot}=5.3\times10^{-3}$ M, T=298 K.

Determination of extinction coefficients

[2]$^{3+}$ in H_2O: A stock solution ***α*** of [**2**]Cl_3 in H_2O (1.2 mg in 10 mL H_2O, 1.0 ×10^{-4} M) was prepared. Four samples containing 2.5 mL, 1.7 mL, 1.1 mL, or 0.7 mL, of solution **α** were prepared in volumetric flasks and the volume of each solution was completed to 5.00 mL by MilliQ H_2O in the dark, to reach concentrations of 5.0×10^{-5} M, 3.0×10^{-5} M, 2.2×10^{-5} M, and 1.5×10^{-5} M, respectively. The UV-vis spectrum of 3 mL of each sample was measured and the extinction coefficient of [**2**]$^{3+}$ in H_2O was obtained from the slope of the plot of absorbance *versus* concentration at each wavelength. The value of extinction coefficients at λ_{max}=570 nm and at λ=500 nm were found to be 44000 L·mol^{-1}·cm^{-1} and 6550 L·mol^{-1}·cm^{-1}, respectively (R^2=0.9999).

[7]$^{3+}$ in H_2O: photoconversion of [**2**]$(PF_6)_3$ in acetone-d4:D_2O(90:10) in a NMR tube (λ_{irr}=452 nm) resulted in the production of compound [**7**]$^{3+}$ in situ, as proven by ^{1}H NMR spectroscopy (see Figure S7). MS analysis showed two peaks at 339.6 and 503.2 for [Ru(**4**)(bpy)(OD_2)]$^{3+}$ ([**7**−3Cl]$^{3+}$) and [Ru(**4**)(bpy)(OD)]$^{2+}$ ([**7**−3Cl−D]$^{2+}$), respectively. Full photoconversion into [**7**]$(PF_6)_3$ was obtained by leaving the tube two days under the sun light. After evaporation of acetone the photoproduced complex [**7**]$^{3+}$ was diluted to 5.0 mL by adding MilliQ water (solution **β**, 1.7 mg, 2.4×10^{-4} M). Five UV-vis cuvettes containing x mL **β**, and 3.0-x mL H_2O were prepared (x: 0.50 ml, 0.33 ml, 0.22 ml, 0.15 ml, and 0.010 ml). The concentrations in the samples were 4.0×10^{-5} M, 2.7×10^{-5} M, 1.8×10^{-5} M, 1.2×10^{-5} M, 7.9×10^{-6} M, and 4.6×10^{-5} M, respectively. Absorbance spectra were measured for all samples and the extinction coefficient of [**7**]$^{3+}$ in water was obtained from the slope of the plot of absorbance *versus* concentration at each wavelength. The value of extinction coefficients at λ_{max}=570 nm and at λ=500 nm were found to be 60000 L·mol^{-1}·cm^{-1} and 9900 L·mol^{-1}·cm^{-1}, respectively (R^2=0.9999).

Extinction coefficients for [Ru(terpy)(bpy)(Hmte)]$^{2+}$ ([**1**]$^{2+}$) and [Ru(terpy)(bpy)(OH_2)]$^{2+}$ ([**8**]$^{2+}$) were obtained as described in previous work .[1]

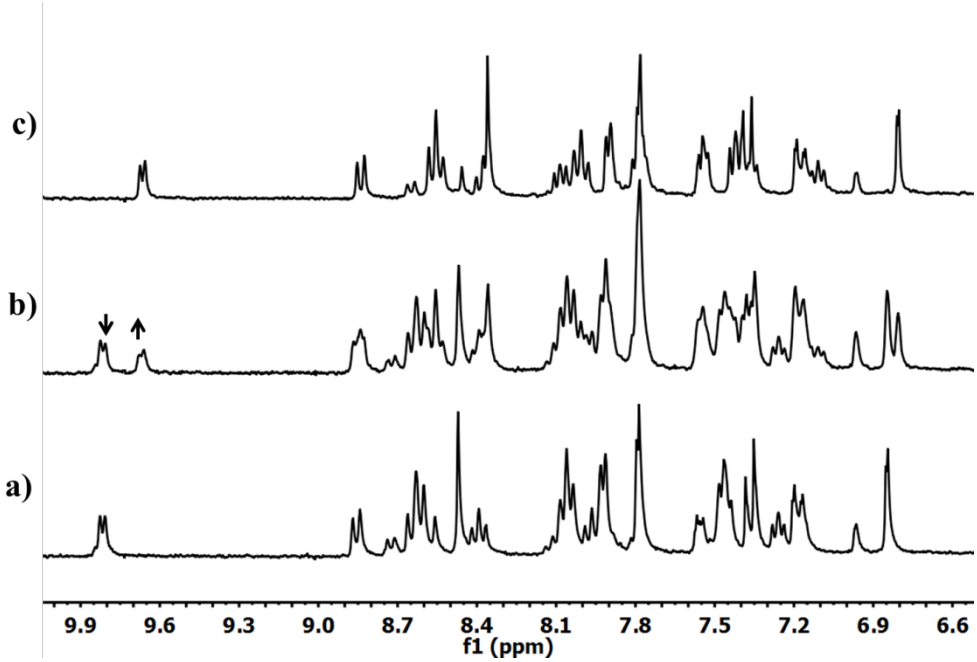

Figure S7. ^{1}H NMR spectra of [**2**](PF$_6$)$_3$ (region 10–6.6 ppm) in acetone-d6/D$_2$O (90:10) (a) before irradiation and in the dark; (b) after 4 h irradiation with yellow light (λ_e=570 nm, $\Delta\lambda_{1/2}$=8.9 nm; the solution contains a mixture of [**2**]$^{3+}$ and [Ru(**4**)(bpy)(OD)]$^{2+}$; and (c) after leaving under sun light for 2 days; full photoconversion to the aqua compound [**7**]$^{3+}$ was reached. Conditions: $[Ru]_{tot}$=2.0×10^{-3} M, T=298 K.

Photon flux determination

Photon flux for the irradiation setup at 452 nm was measured using the ferrioxalate actinometer. [2] However, the ferrioxalate actinometer is not suited for 570 nm photons, so that an indirect method was used. The light power (in $mW \cdot cm^{-2}$) at 452 nm (I_{452}) and 570 nm (I_{570}) was measured using an OPHIR Nova power meter. Knowing the photon flux at 452 nm (Φ_{452}), the photon flux at 570 nm (Φ_{570}) was calculated using Equation S1. In this equation E_λ is the photon energy at 452 nm ($E_{452}=4.4\times10^{-19}$ J) and at 570 nm ($E_{570}=3.5\times10^{-19}$ J). The photon flux at 570 nm was found to be 5.3×10^{-9} Einstein.s^{-1}.

$$\frac{I_{452}}{I_{572}} = \frac{\Phi_{452}\times E_{452}}{\Phi_{570}\times E_{570}} \qquad \textbf{(Equation S1)}$$

Quantum Yield measurements

The abosrbance($A^{\lambda}_{t_j}$) of a solution containing RuHmte ($[\mathbf{2}]^{3+}$ or $[\mathbf{1}]^{2+}$) and $RuOH_2$ ($[\mathbf{7}]^{3+}$ or $[\mathbf{8}]^{2+}$) at each wavelength and at each irratiation time (t_j) is given by Equation S2. *L'*, in this equation, is the pathlength for absorbance measurement (see Figure S9), *[RuHmte]* and *[$RuOH_2$]* are the concentrations of the RuHmte complex ($[\mathbf{2}]^{3+}$ or $[\mathbf{1}]^{2+}$) and $RuOH_2$ complex ($[\mathbf{7}]^{3+}$ or $[\mathbf{8}]^{2+}$), respectively.

$$A^{\lambda}_{t_j} = L'\times\varepsilon^{\lambda}_{RuHmte}\cdot[RuHmte]_{t_j} + L'\cdot\ \varepsilon^{\lambda}_{RuOH2}\times[RuOH_2]_{t_j} \quad \textbf{(Equation S2)}$$

At t_∞ (full photoconversion):

$$A^{\lambda}_{t\infty} = L'\times\varepsilon^{\lambda}_{RuOH2}\times[Ru]_{tot} \quad \textbf{(Equation S3)}$$

Where *$[Ru]_{tot}$* is the total Ru concentration. If we replace *[$RuOH_2$]* by *$[Ru]_{tot}-[RuHmte]$* in Equation S2, *[RuHmte]* can be obtained from Equation S4.

$$[RuHmte] = \frac{A^{\lambda}_{t_j} - A^{\lambda}_{t\infty}}{L'\times(\varepsilon^{\lambda}_{RuHmte} - \varepsilon^{\lambda}_{RuOH2})} \qquad \textbf{(Equation S4)}$$

When the irradiation wavelength is not close to the isosbestic point, the absorbance at the irradiation wavelength is not constant throughout the whole irradiation period, which must be taken into account. Thus the procedure below was applied to calculate the photosubstitution quantum yields. [3]

The average absorbance between two consecutive UV-vis measurements at t_j and t_{j+1}, at the irradiation wavelength λ_e (452 nm or 570 nm) was calculated according to Equation S5.

$$(A_{\lambda e})_{ave} = \frac{(A_{\lambda e})_j + (A_{\lambda e})_{j+1}}{2} \qquad \textbf{(Equation S5)}$$

The number of moles of photons absorbed by the ruthenium complex RuHmte between two consecutive UV-vis measurements ($\Delta t = t_{j+1} - t_j$) was calculated according to Equation S6. In this Equation $\Phi_{\lambda e}$ is the photon flux

at irradiation wavelength (λ_e) and $(1-10^{-3\times(A_{\lambda e})_{gemi}})$ is the photon absorption probability. As shown in Figure S9, the sample was irradiated from the top of the UV-vis cuvette (irradiation pathlength: L=3 cm) while the absorbance was measured perpendicular to the light irradiation direction (absorbance pathlength L'=1 cm). Thus $(A_{\lambda e})_{gemi}$ is multiplied by 3 in order to obtain the probability of photon absorption.

$$q_j = \left(\frac{A_{RuSRR'}}{(A_{\lambda e})_{ave}}\right)_j \times\left(1-10^{-3(A_{\lambda e})_{ave}}\right)\times\Phi_{\lambda e}\times\Delta t \quad \textbf{(Equation S6)}$$

The total number of moles of photons absorbed by the product at time t since t=0, $Q(t)$, was calculated according to Equation S7, where j is summed on all measurements times t_j until t.

$$Q(t) = \sum_j q_j \quad \textbf{(Equation S7)}$$

The quantum yield was obtained from the slope of a plot of number of moles of RuHmte (n_{RuHmte}) *vs.* Q (see Figure 5b).

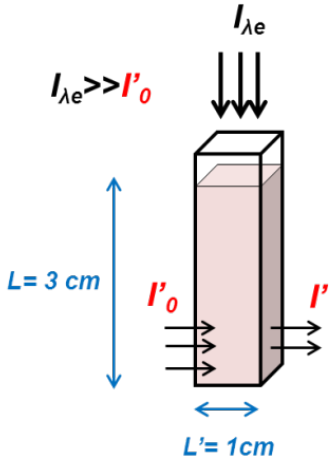

Figure S8. Irradiation of a solution in a UV-vis cuvette is done in situ, perpendicular to the optical axis of the spectrophotometer. Irradiation pathlength=L, UV-vis absorption pathlength=L', $\Phi_{\lambda e}$: photon flux at the irradiation wavelength λ_e, $I_{\lambda e}$: light power at irradiation wavelength λ_e. I': UV-vis light beam intensity measured by the spectrophotometer.

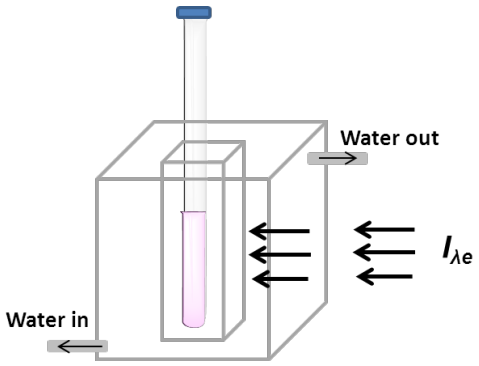

Figure S9. Irradiation of [**2**]Cl_3 in water from the side of an NMR tube. The NMR tube was hold in a sample holder that was equipped with a water circulator to keep the temperature constant.

Förster distance R_0 and spectral overlap calculations

Overlap integral which expresses the degree of spectral overlap between the donor ([**4**]$^{+}$) emission and the acceptor ([**1**]$^{2+}$) was calculated using Equation S8. In equation S8 $F_D(\lambda)$ is the donor emission intensity at wavelength λ normalized to an area of 1, ε_A is the extinction coefficient (in $M^{-1}\cdot cm^{-1}$) of the acceptor at wavelength λ. If the wavelength λ is expressed in cm, then the unit of J_{DA} is $M^{-1}\cdot cm^{3}$. A plot of $J(\lambda)$, defined according to Equation S9, is shown in Figure S10.

$$J_{DA} = \frac{\int F_D(\lambda)\cdot\varepsilon_A(\lambda)\cdot\lambda^4 d\lambda}{\int F_D(\lambda) d\lambda} \qquad \text{(Equation S8)}$$

$$J(\lambda) = F_D(\lambda)\cdot\varepsilon_A(\lambda)\cdot\lambda^4 \qquad \text{(Equation S9)}$$

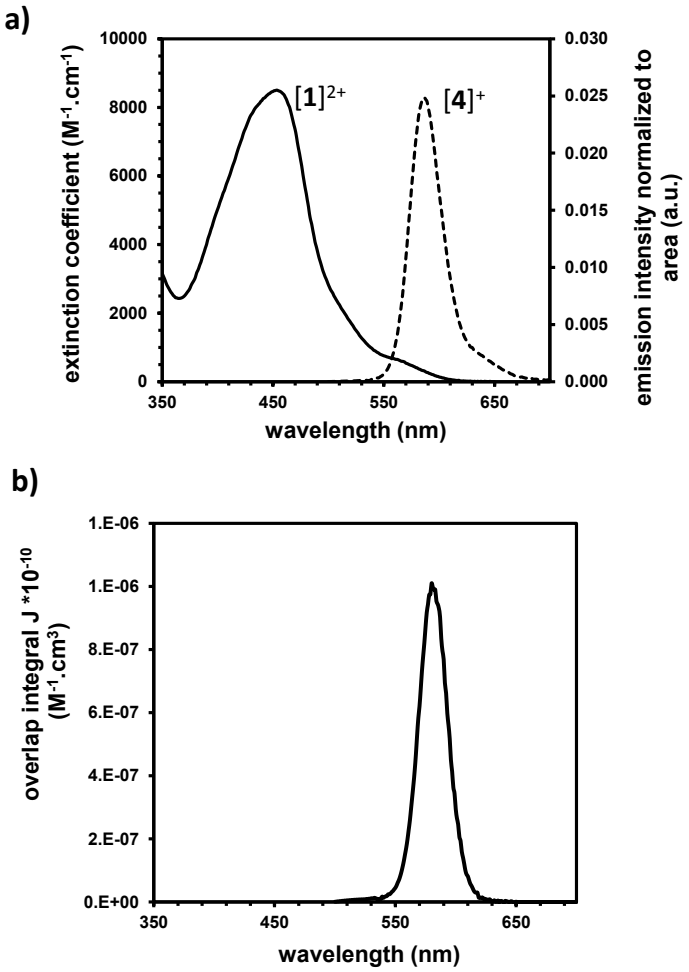

Figure S10. a) Absorption spectrum of compound $[\mathbf{1}]^{2+}$ (left axis) and normalized emission spectrum of [**4**]Cl (right axis) in water. b) Overlap *J(λ)* between the donor emission ([**4**]Cl) and the acceptor absorption ($[\mathbf{1}](BF_4)_2$) in Figure S10a. All spectra measured in water at pH 7.

DFT calculations

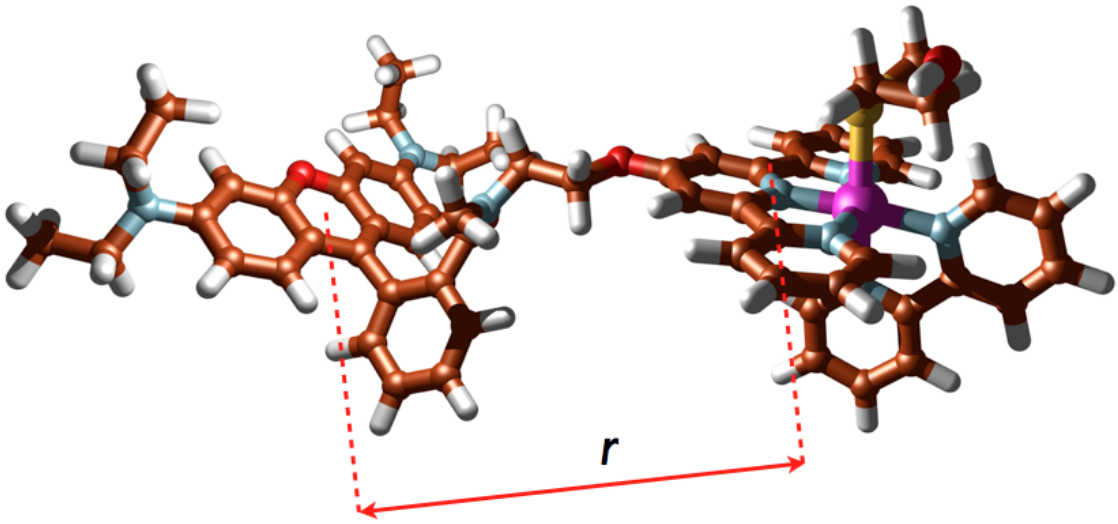

Figure S11. DFT-minimized geometry of the dyad $[\mathbf{2}]^{3+}$.

Table S1. Z-matrix (Å) of the DFT-minimized model of dyad $[2]^{3+}$.

c

c	1 cc2		
c	2 cc3	1 ccc3	
c	3 cc4	2 ccc4	1 dih4
o	4 oc5	3 occ5	2 dih5
c	5 co6	4 coc6	3 dih6
c	4 cc7	3 ccc7	2 dih7
c	7 cc8	4 ccc8	3 dih8
c	8 cc9	7 ccc9	4 dih9
c	9 cc10	8 ccc10	7 dih10
c	1 cc11	6 ccc11	5 dih11
c	11 cc12	1 ccc12	6 dih12
c	12 cc13	11 ccc13	1 dih13
c	13 cc14	12 ccc14	11 dih14
c	2 cc15	3 ccc15	10 dih15
c	15 cc16	2 ccc16	3 dih16
c	16 cc17	15 ccc17	2 dih17
c	17 cc18	16 ccc18	15 dih18
c	18 cc19	17 ccc19	16 dih19
c	19 cc20	18 ccc20	17 dih20
c	16 cc21	15 ccc21	20 dih21
o	21 oc22	16 occ22	15 dih22
n	8 nc23	9 ncc23	10 dih23
c	23 cn24	8 cnc24	9 dih24

c 24 cc25 23 ccn25 8 dih25
n 13 nc26 14 ncc26 6 dih26
c 26 cn27 13 cnc27 14 dih27
c 27 cc28 26 ccn28 13 dih28
n 21 nc29 16 ncc29 15 dih29
c 29 cn30 21 cnc30 16 dih30
c 29 cn31 21 cnc31 22 dih31
c 31 cc32 29 ccn32 21 dih32
o 32 oc33 31 occ33 29 dih33
c 33 co34 32 coc34 31 dih34
c 34 cc35 33 cco35 32 dih35
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c 38 cc39 37 ccn39 36 dih39
ru 37 run40 36 runc40 35 dih40
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h  30 hc115   29 hcn115   31 dih115
h  30 hc116   29 hcn116   31 dih116
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h  24 hc118   23 hcn118    8 dih118
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h  25 hc120   24 hcc120   23 dih120
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h  73 hc125   72 hcc125   23 dih125
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h  27 hc128   26 hcn128   13 dih128
h  28 hc129   27 hcc129   26 dih129
h  28 hc130   27 hcc130   26 dih130
h  28 hc131   27 hcc131   26 dih131
h  70 hc132   26 hcn132   13 dih132
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h  71 hc134   70 hcc134   26 dih134
h  71 hc135   70 hcc135   26 dih135
h  71 hc136   70 hcc136   26 dih136
variables
cc2          1.405414   ccc36      118.939   dih69      143.891   hcc103     109.401
cc3          1.435734   dih36     -179.375   cn70       1.489817  dih103      23.606
ccc3       119.017      nc37       1.368226  cnc70    121.116     hc104       1.087471
cc4          1.42916    ncc37    119.944     dih70        4.495   hcc104    118.858
ccc4       119.365      dih37     -0.748     cc71       1.545074  dih104      6.176
dih4        -6.346      cn38       1.36073   ccn71    113.119     hc105       1.085726
oc5          1.393082   cnc38    122.3       dih71       73.225   hcc105    120.527
occ5       120.373      dih38      0.098     cn72       1.494729  dih105    179.265
dih5        -0.777      cc39       1.400041  cnc72    118.198     hc106       1.08783
co6          1.389247   ccn39    120.188     dih72       98.62    hcc106    119.782
coc6       120.526      dih39      0.681     cc73       1.531214  dih106    179.515
dih6         7.359      run40      2.005031  ccn73    115.87      hc107       1.086807
cc7          1.392018   runc40   119.022     dih73       47.966   hcc107    119.179
ccc7       122.995      dih40   -176.595     hc74       1.082954  dih107    179.19
dih7       178.194      sru41      2.587559  hcn74    116.554     hc108       1.083718
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cc8	1.41263	srun41	83.521	dih74	1.873	hcc108	119.762
ccc8	119.551	dih41	86.121	hc75	1.084096	dih108	6.73
dih8	-4.779	cs42	1.904563	hcc75	121.181	hc109	1.085878
cc9	1.431492	csru42	119.43	dih75	-179.237	hcc109	119.571
ccc9	118.337	dih42	101.69	hc76	1.084926	dih109	177.515
dih9	2.534	cc43	1.539201	hcc76	120.442	hc110	1.083757
cc10	1.384106	ccs43	116.348	dih76	179.409	hcc110	120.423
ccc10	121.375	dih43	70.27	hc77	1.084696	dih110	177.222
dih10	2.844	oc44	1.452205	hcc77	120.235	hc111	1.081509
cc11	1.433833	occ44	109.724	dih77	179.824	hcc111	118.054
ccc11	115.657	dih44	161.568	hc78	1.082019	dih111	-0.691
dih11	177.128	cc45	1.480807	hcc78	120.727	hc112	1.080564
cc12	1.371092	ccn45	113.072	dih78	179.375	hcc112	119.736
ccc12	121.738	dih45	3.747	hc79	1.083479	dih112	177.08
dih12	2.674	nc46	1.386319	hcc79	122.41	hc113	1.081724
cc13	1.448097	ncc46	115.661	dih79	179.482	hcc113	119.18
ccc13	121.787	dih46	-2.927	hc80	1.085275	dih113	-178.565
dih13	1.275	cn47	1.359854	hcc80	119.564	hc114	1.090258
cc14	1.427784	cnc47	119.066	dih80	-179.709	hcn114	110.776
ccc14	117.245	dih47	179.851	hc81	1.085895	dih114	165.521
dih14	-4.217	cc48	1.400759	hcc81	120.576	hc115	1.09833
cc15	1.493032	ccn48	122.312	dih81	179.359	hcn115	109.313
ccc15	118.036	dih48	-0.115	hc82	1.085492	dih115	46.546
dih15	-7.05	cc49	1.40444	hcc82	119.698	hc116	1.100569
cc16	1.418377	ccc49	119.026	dih82	-179.721	hcn116	111.994
ccc16	123.306	dih49	0.19	hc83	1.084947	dih116	-74.145
dih16	-111.105	cc50	1.403739	hcn83	116.504	hc117	1.096834
cc17	1.410457	ccc50	118.991	dih83	-1.471	hcn117	107.938
ccc17	119.12	dih50	-0.29	hc84	1.082371	dih117	-30.208
dih17	172.681	cc51	1.479858	hcn84	116.737	hc118	1.104833
cc18	1.399769	ccn51	113.429	dih84	1.875	hcn118	111.799
ccc18	121.582	dih51	-2.186	hc85	1.084794	dih118	88.206
dih18	0.993	nc52	1.387055	hcc85	121.217	hc119	1.09628
cc19	1.405458	ncc52	115.71	dih85	179.471	hcc119	109.974
ccc19	119.389	dih52	2.314	hc86	1.084279	dih119	168.488
dih19	-0.49	cn53	1.358963	hcc86	120.335	hc120	1.095599
cc20	1.402194	cnc53	118.836	dih86	-179.844	hcc120	112.492
ccc20	119.644	dih53	-179.403	hc87	1.082905	dih120	-71.991
dih20	-0.322	cc54	1.399961	hcc87	120.414	hc121	1.095893
cc21	1.510947	ccn54	122.47	dih87	-179.683	hcc121	109.889
ccc21	125.205	dih54	-0.351	hc88	1.083224	dih121	49.225

dih21	172.986	cc55	1.405408	hcc88	119.798	hc122	1.10776
oc22	1.258785	ccc55	119.054	dih88	179.224	hcn122	108.334
occ22	121.16	dih55	-0.271	hc89	1.084482	dih122	-75.199
dih22	-61.154	cc56	1.403335	hcc89	120.683	hc123	1.091836
nc23	1.410664	ccc56	118.886	dih89	179.319	hcn123	107.234
ncc23	120.343	dih56	0.647	hc90	1.084699	dih123	169.821
dih23	-177.793	nru57	2.068719	hcc90	119.863	hc124	1.096636
cn24	1.490037	nrun57	90.823	dih90	179.822	hcc124	108.588
cnc24	116.543	dih57	-96.006	hc91	1.078837	dih124	-179.001
dih24	-42.201	cn58	1.377015	hcn91	116.179	hc125	1.095698
cc25	1.539715	cnru58	115.462	dih91	-0.532	hcc125	111.039
ccn25	111.227	dih58	-97.987	hc92	1.090789	dih125	62.268
dih25	-148.954	cc59	1.402874	hcs92	107.176	hc126	1.095866
nc26	1.362411	ccn59	120.961	dih92	58.27	hcc126	112.416
ncc26	121.884	dih59	178.22	hc93	1.091024	dih126	-60.236
dih26	-177.426	cc60	1.398834	hcs93	106.758	hc127	1.096163
cn27	1.486573	ccc60	119.876	dih93	175.85	hcn127	109.53
cnc27	121.06	dih60	0.276	hc94	1.09039	dih127	47.141
dih27	177.59	cc61	1.405044	hcs94	112.92	hc128	1.093476
cc28	1.5438	ccc61	118.859	dih94	-63.097	hcn128	107.448
ccn28	113.002	dih61	0.583	hc95	1.094175	dih128	161.854
dih28	-77.234	cc62	1.397578	hcs95	104.917	hc129	1.094621
nc29	1.391288	ccc62	119.039	dih95	-169.572	hcc129	110.633
ncc29	117.248	dih62	-0.604	hc96	1.093123	dih129	-60.727
dih29	126.364	cc63	1.469298	hcs96	105.38	hc130	1.095586
cn30	1.473524	ccn63	115.605	dih96	-54.593	hcc130	111.915
cnc30	124.227	dih63	-1.76	hc97	1.092234	dih130	59.885
dih30	-21.589	nc64	1.377629	hcc97	110.77	hc131	1.095973
cn31	1.473803	ncc64	114.937	dih97	47.77	hcc131	110.065
cnc31	118.485	dih64	0.637	hc98	1.099999	dih131	-179.74
dih31	-6.787	cn65	1.360993	hcc98	111.453	hc132	1.093708
cc32	1.546396	cnc65	118.652	dih98	-73.439	hcn132	107.296
ccn32	110.918	dih65	-179.563	ho99	0.978964	dih132	-165.638
dih32	-117.194	cc66	1.396607	hoc99	113.509	hc133	1.096592
oc33	1.482154	ccn66	122.701	dih99	80.508	hcn133	109.267
occ33	108.947	dih66	0.011	hc100	1.098447	dih133	-50.579
dih33	142.66	cc67	1.405536	hco100	108.792	hc134	1.09469
co34	1.371539	ccc67	118.814	dih100	62.867	hcc134	111.879
coc34	118.705	dih67	0.103	hc101	1.099314	dih134	-60.767
dih34	-175.582	cc68	1.401366	hco101	107.93	hc135	1.09576
cc35	1.416894	ccc68	119.004	dih101	-56.779	hcc135	111.015

cco35	116.632	dih68	-0.012	hc102	1.096344	dih135	59.939
dih35	171.503	cs69	1.889671	hcc102	110.111	hc136	1.09634
cc36	1.394742	csru69	118.045	dih102	-95.804	hcc136	110.12
				hc103	1.090688	dih136	179.464

constants

end

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