Supporting information for:

Comparison of rhenium-porphyrin dyads for CO_2 photoreduction: photocatalytic studies and charge separation dynamics studied by time-resolved IR spectroscopy

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Primary data will be made available at DOI: 10.15124/4335e576-3737-4968-841b-076f8a4658ca

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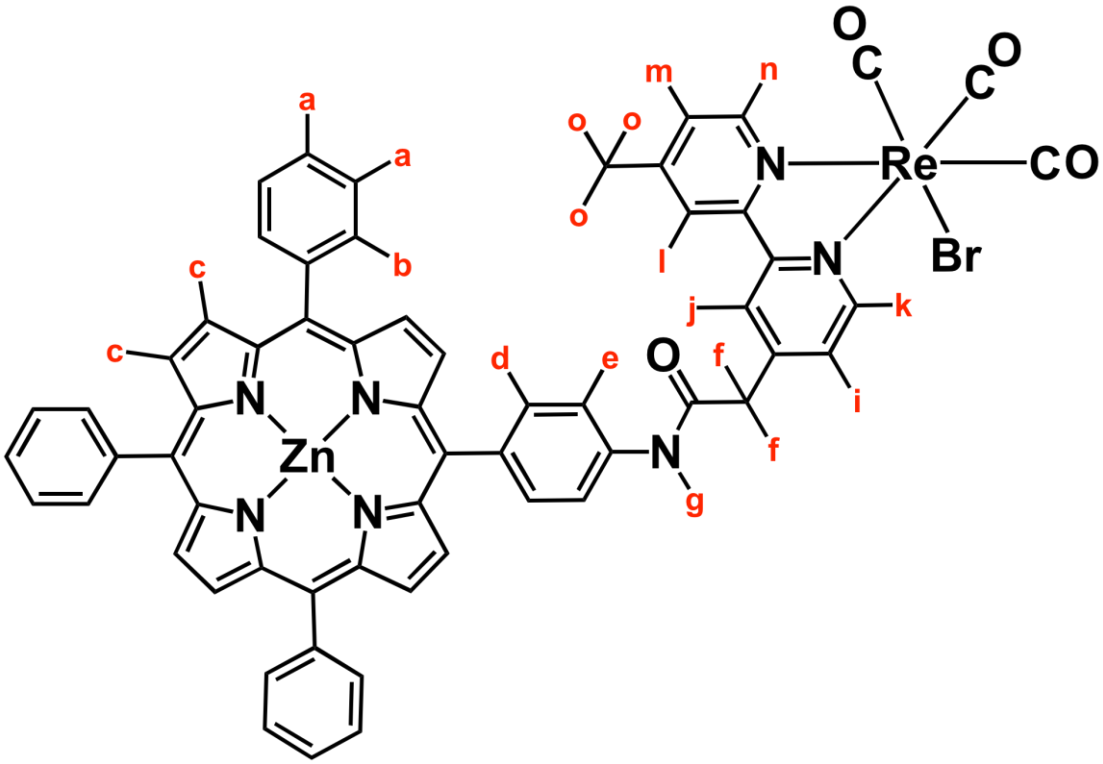

Figure S 1. ^{1}H NMR assignment of **Dyad 3 Br**.

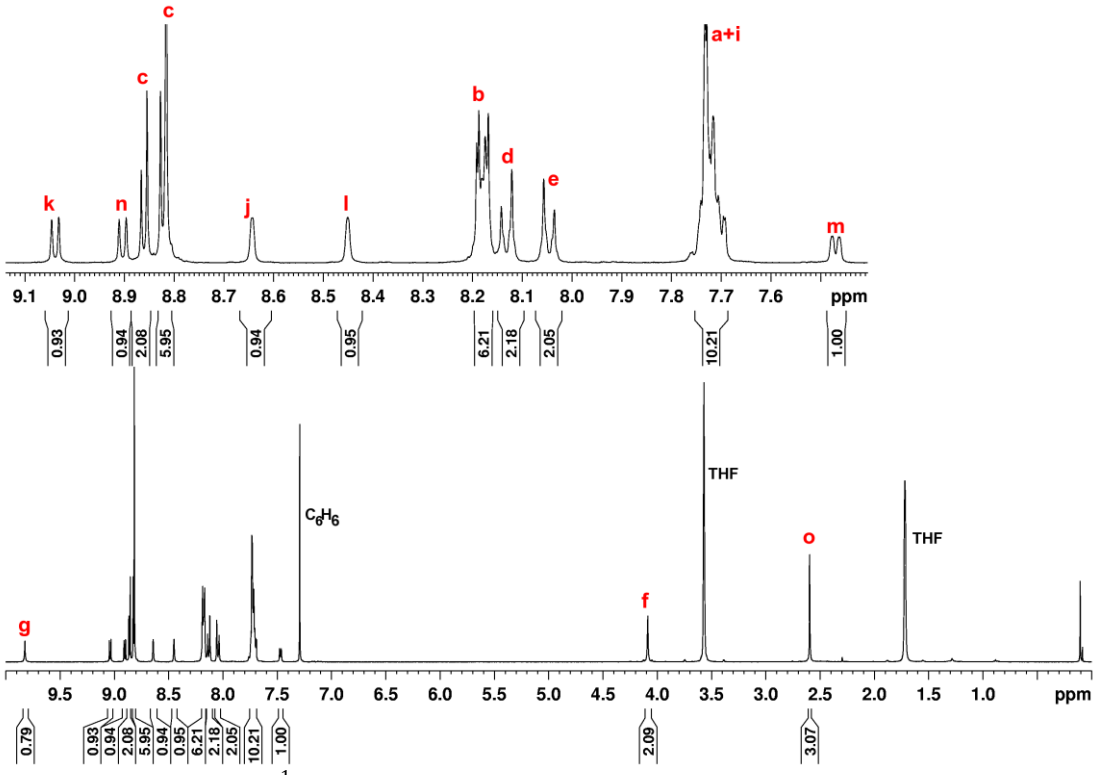

Figure S 2. ^{1}H NMR spectrum of **Dyad 3 Br** (THF-d_8 400 MHz).

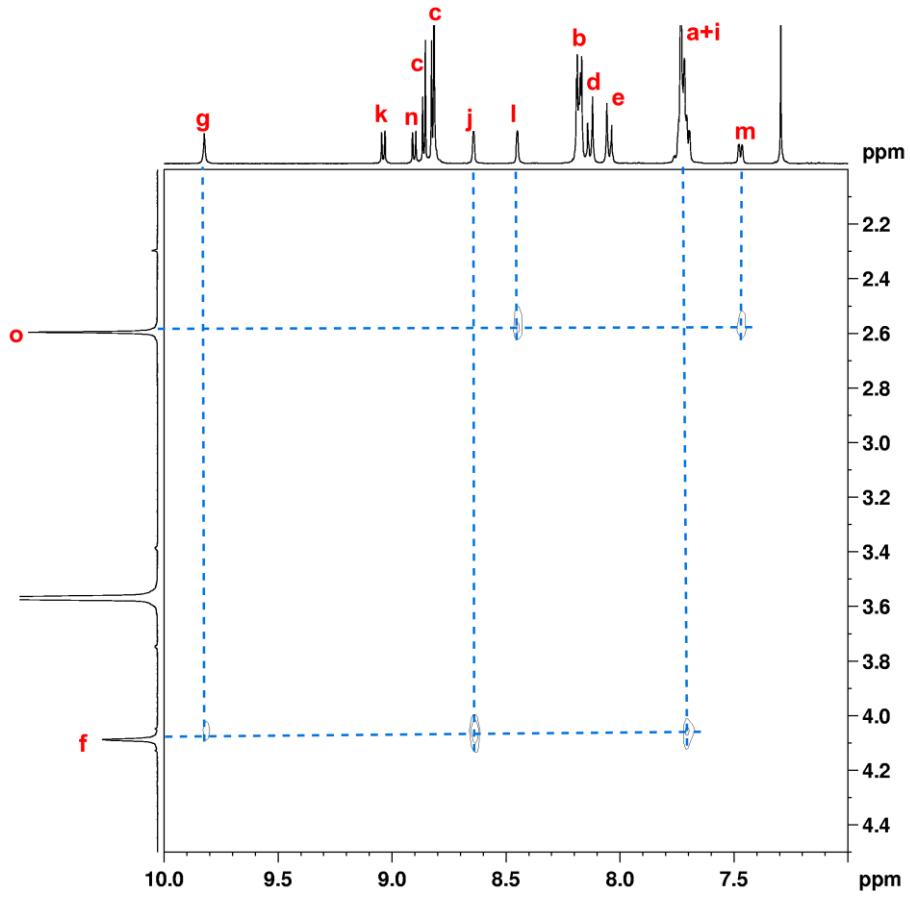

Figure S 3. ^{1}H-^{1}H NOESY spectrum of **Dyad 3 Br** (THF-d_8 400 MHz).

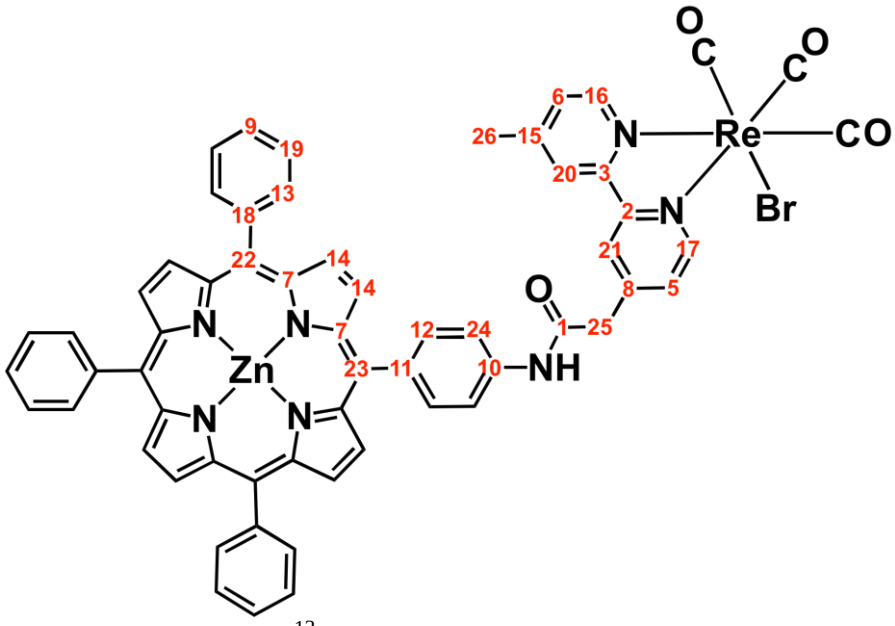

Figure S 4. ^{13}C NMR assignment of **Dyad 3 Br**.

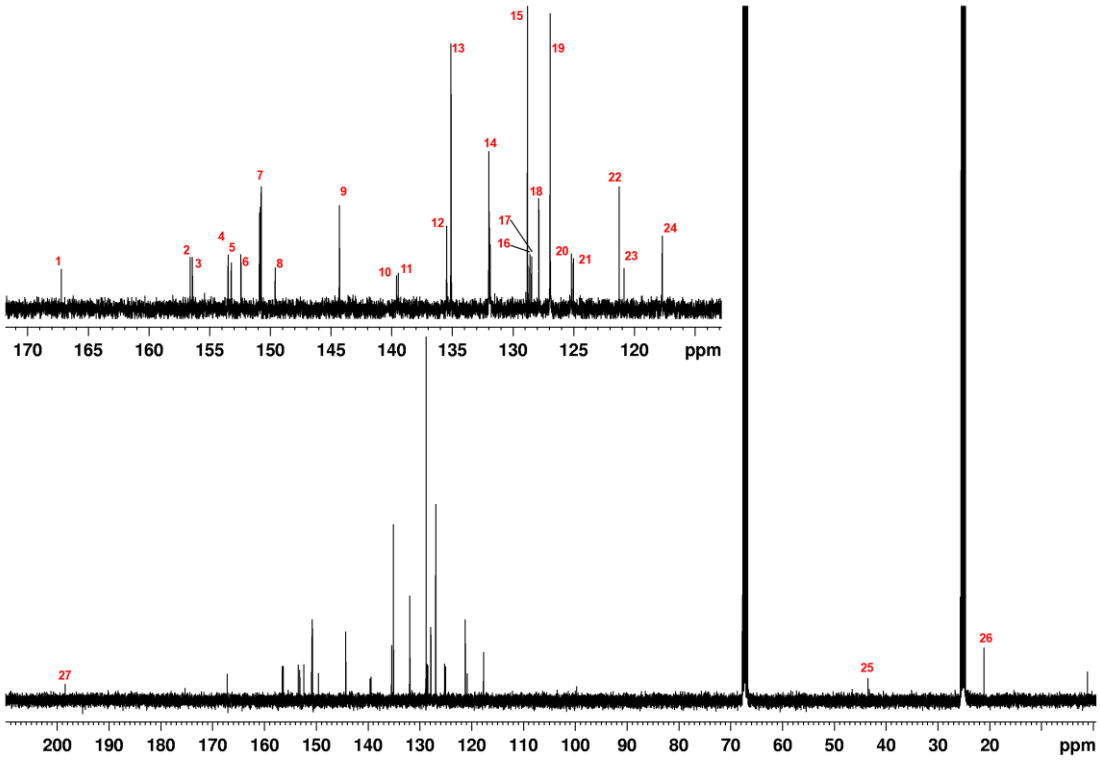

Figure S 5. $^{13}C\{^{1}H\}$ NMR spectrum of **Dyad 3 Br** (THF-d_8 100.6 MHz).

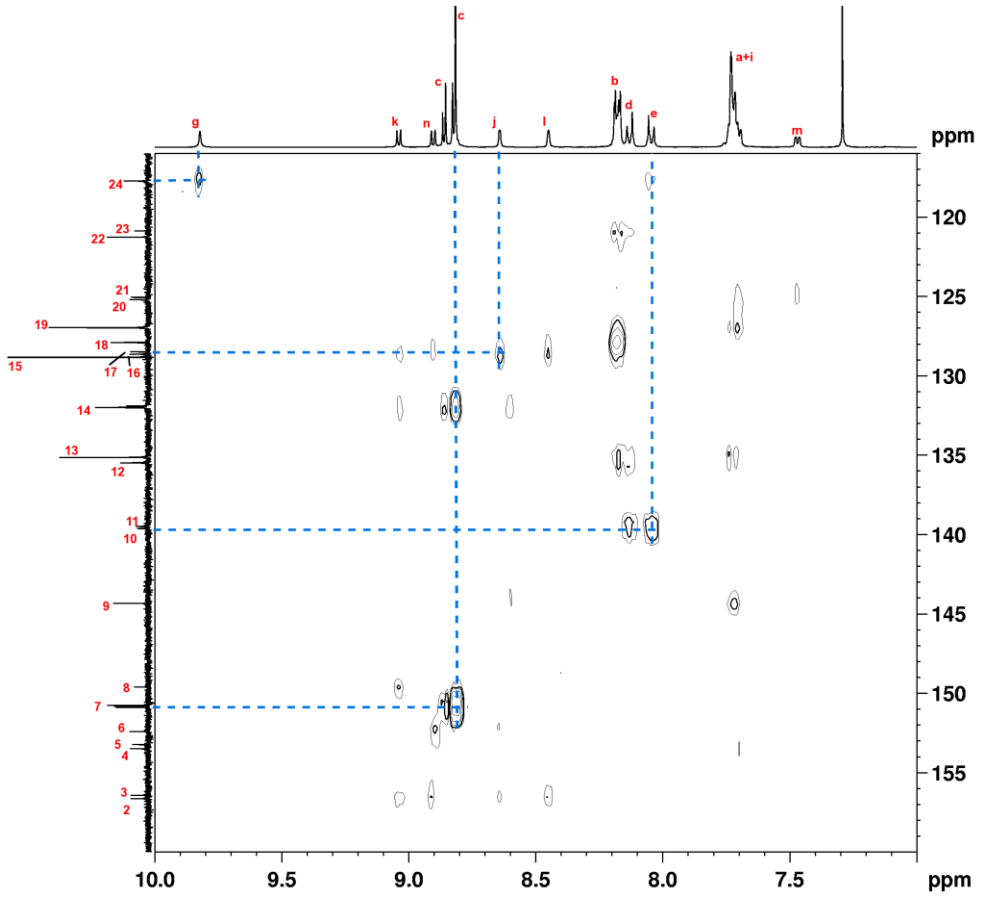

Figure S 6. ^{1}H-^{13}C HMBC NMR spectrum of **Dyad 3 Br** (THF-d_8 400 MHz).

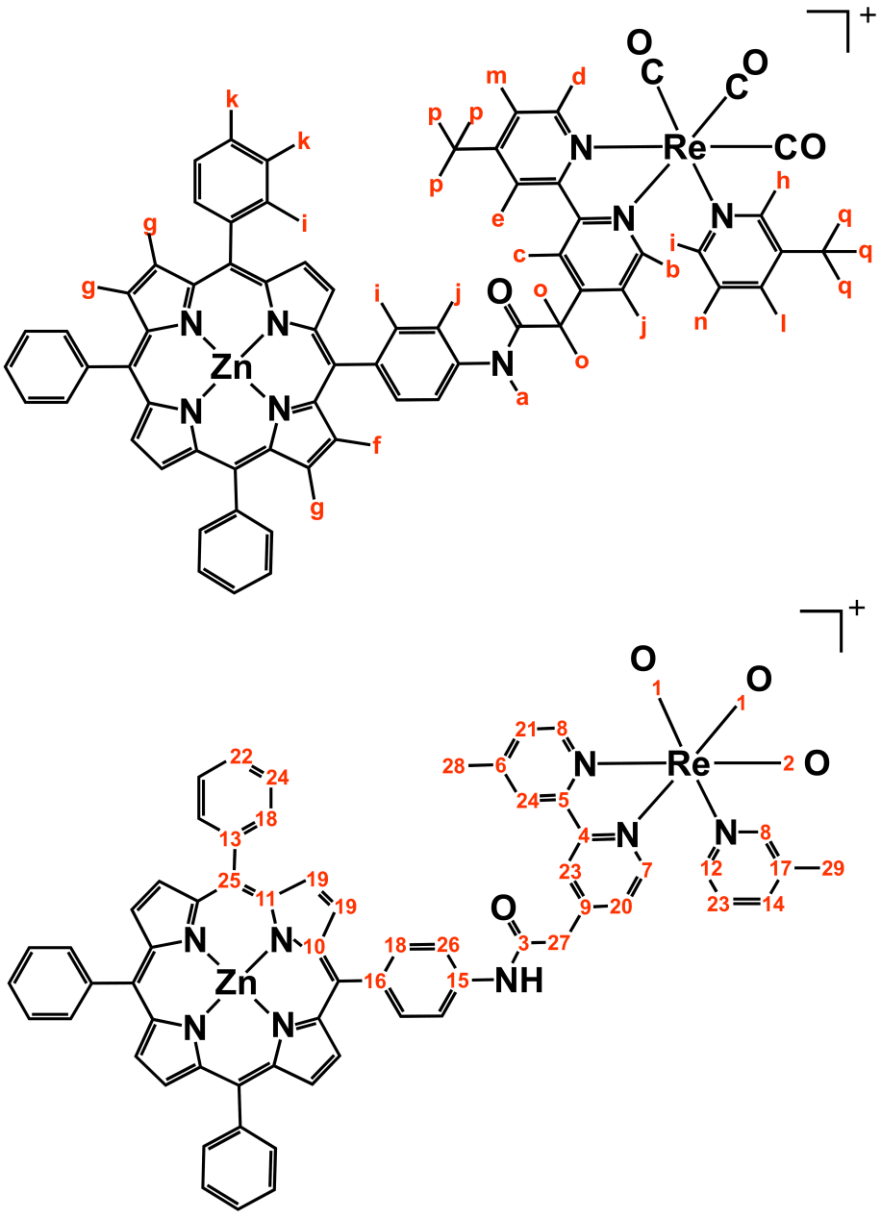

Figure S 7. ^{1}H (top) and ^{13}C (bottom) assignment of **[Dyad 3 pic]OTf**.

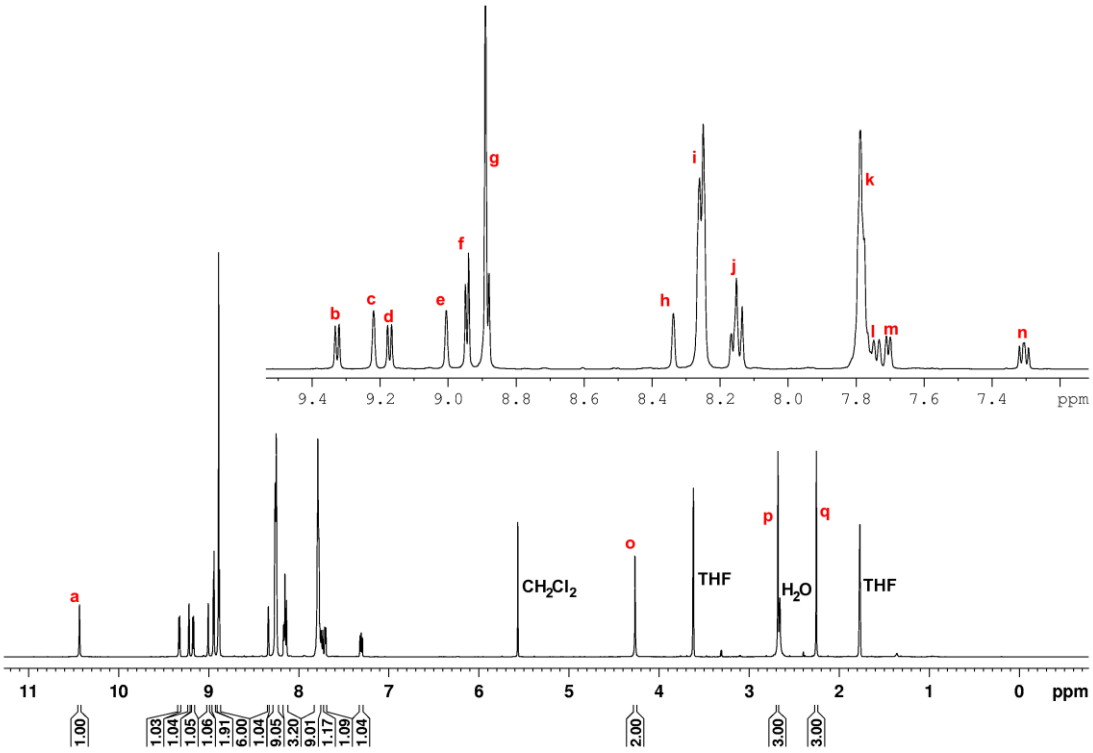

Figure S 8. ^{1}H NMR spectrum of **[Dyad 3 pic]OTf** (THF-d_8 400 MHz).

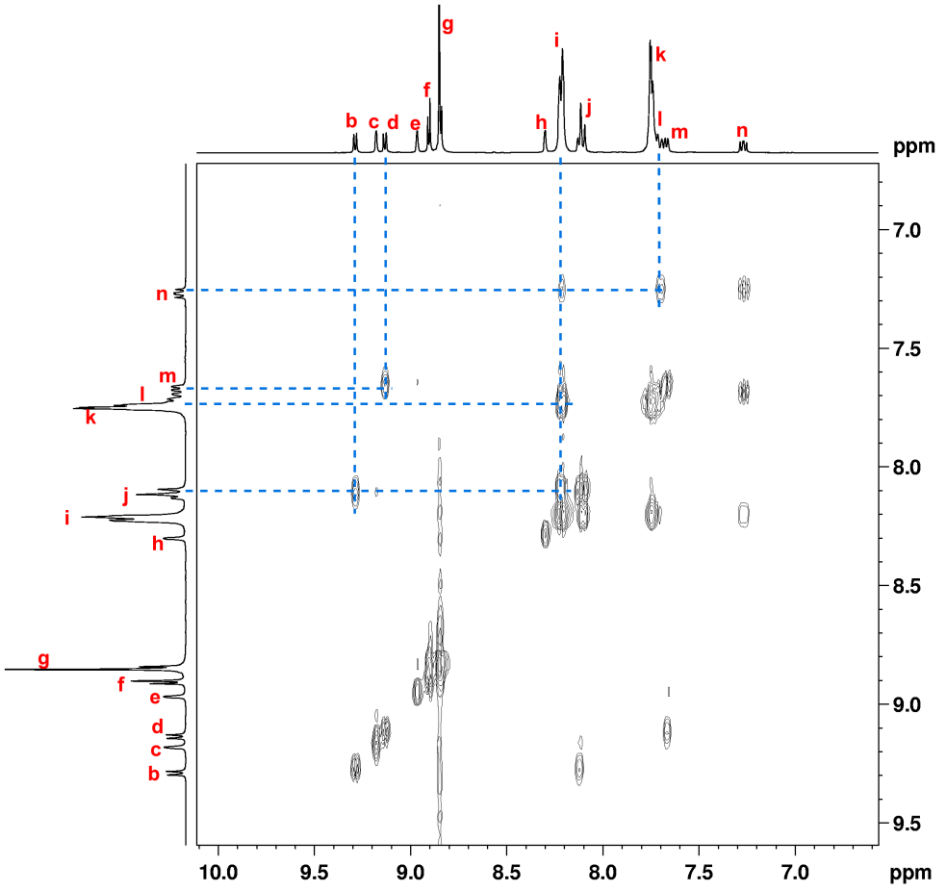

Figure S 9. ^{1}H-^{1}H COSY spectrum of **[Dyad 3 pic]OTf** (THF-d_8 400 MHz).

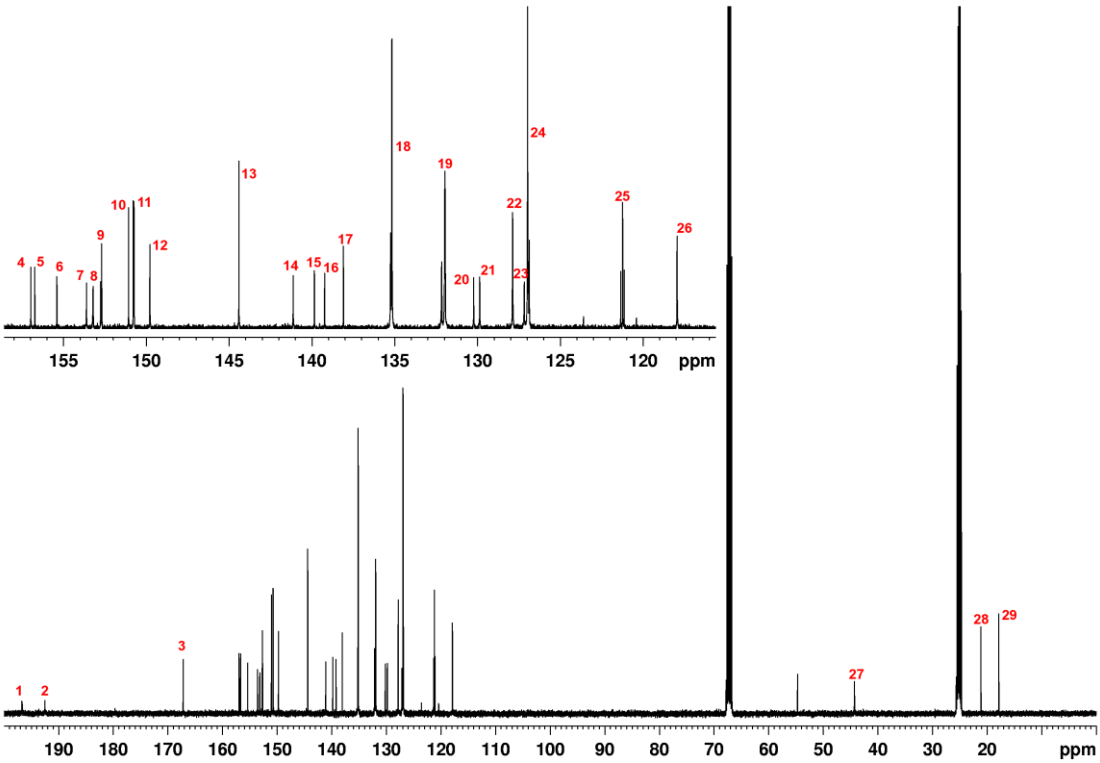

Figure S 10. $^{13}C\{^{1}H\}$ NMR spectrum of **[Dyad 3 pic]OTf** (THF-d_8 100.6 MHz).

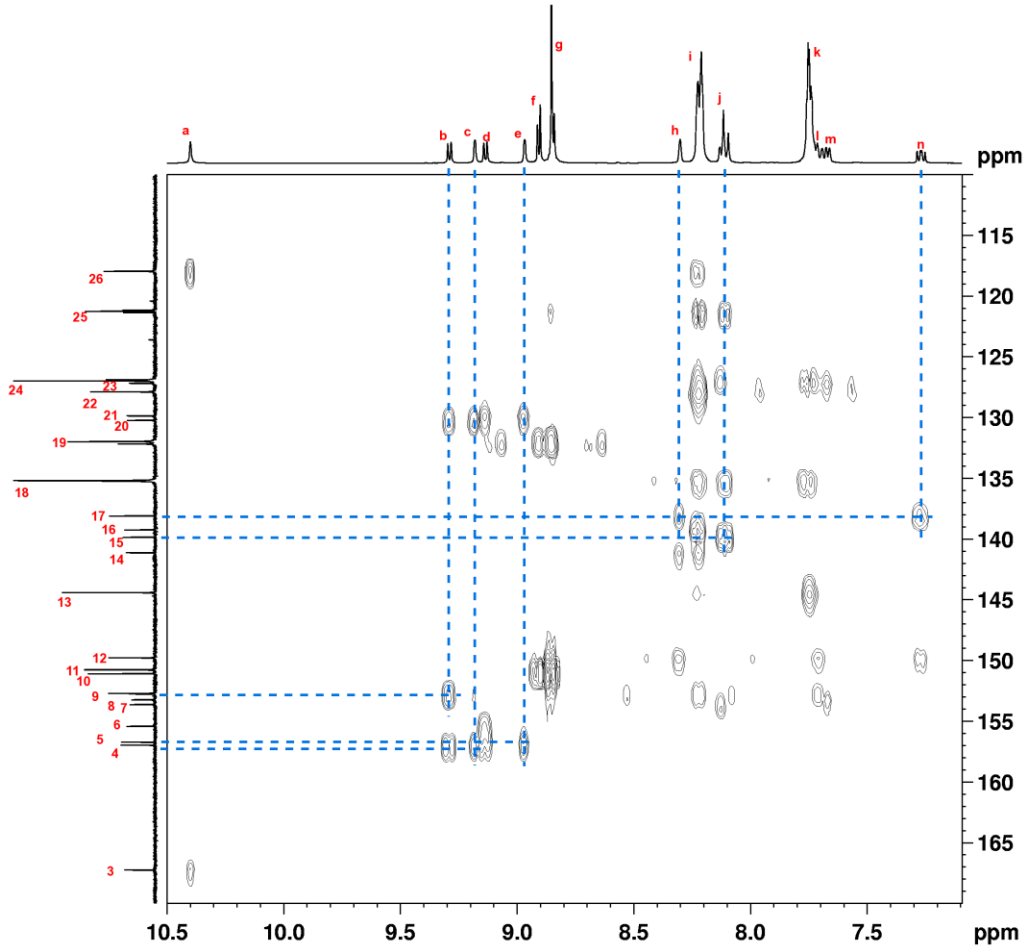

Figure S 11. ^{1}H-^{13}C HMBC NMR spectrum of **[Dyad 3 pic]OTf** (THF-d_8 400 MHz).

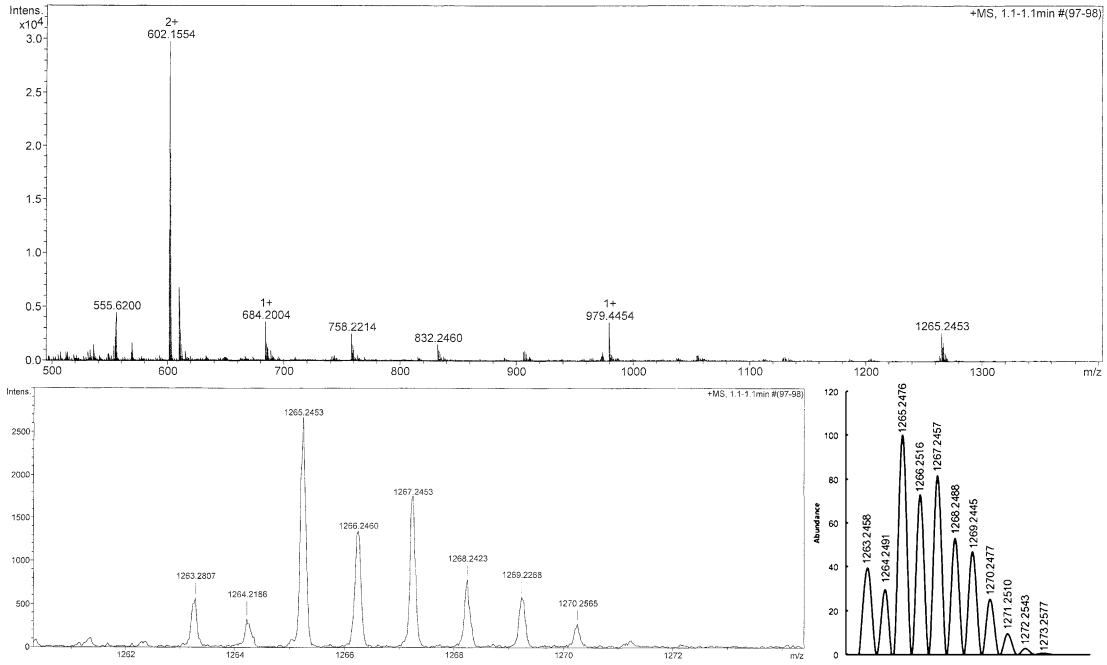

Figure S 12 ESI-MS of **[Dyad 3 pic]OTf**: Top is full mass range, bottom left is expansion of M^+, bottom right is the calculated isotope pattern.

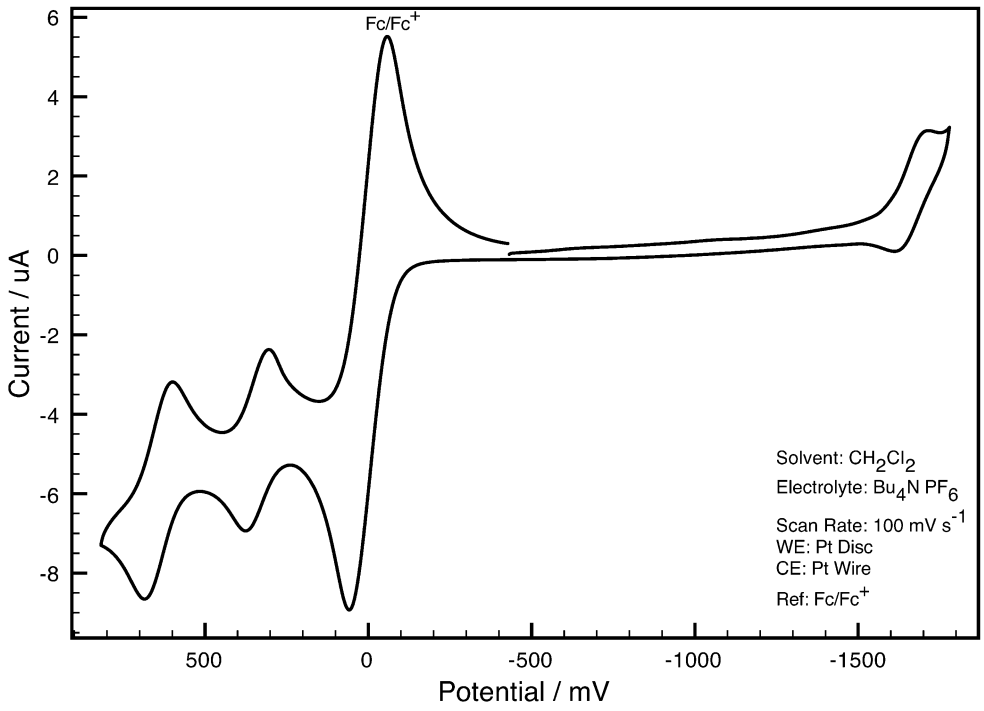

Figure S 13. Cyclic voltammogram of **[Dyad 3 pic]OTf**

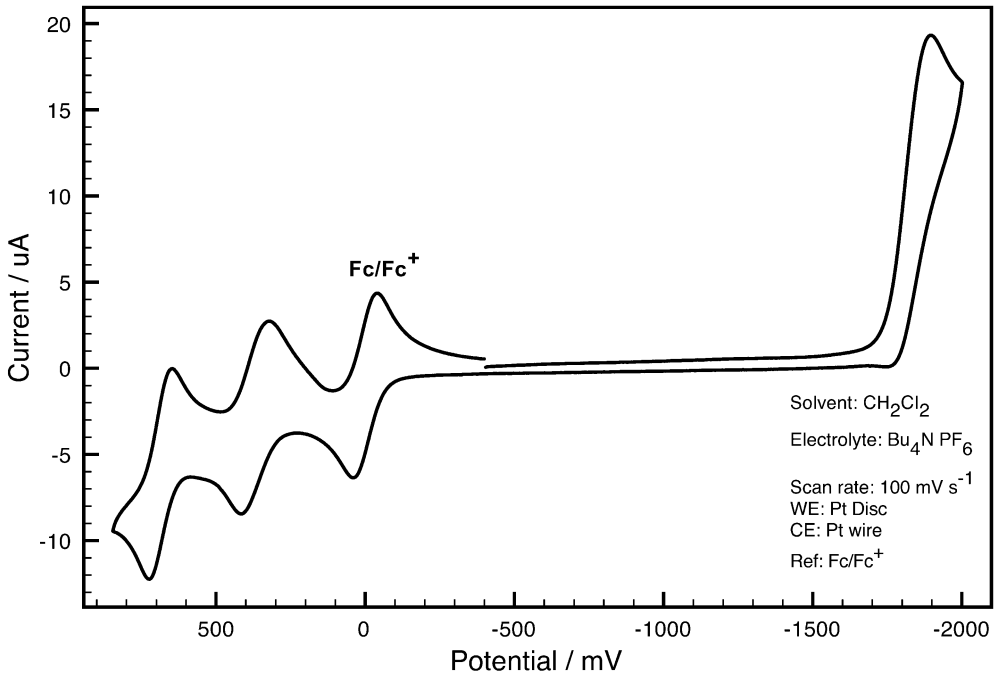

Figure S 14. Cyclic voltammogram of **Dyad 3 Br**

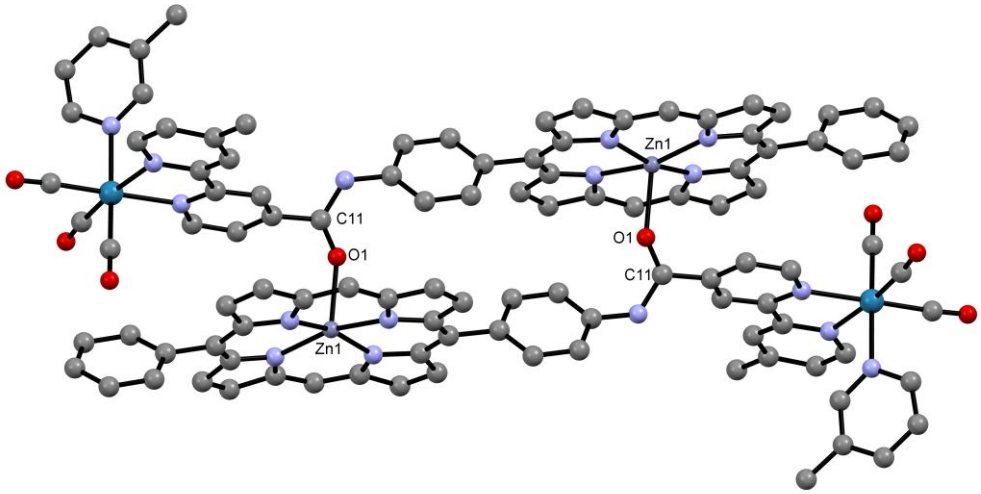

Figure S 15. X-ray crystal structure of **[Dyad 1 pic]PF_6**. Hydrogen atoms and 2 porphyrin phenyls, PF_6 counterion and solvent of crystallization omitted for clarity. Selected bond length (Å): Zn(1)-O(1): 2.216(4).

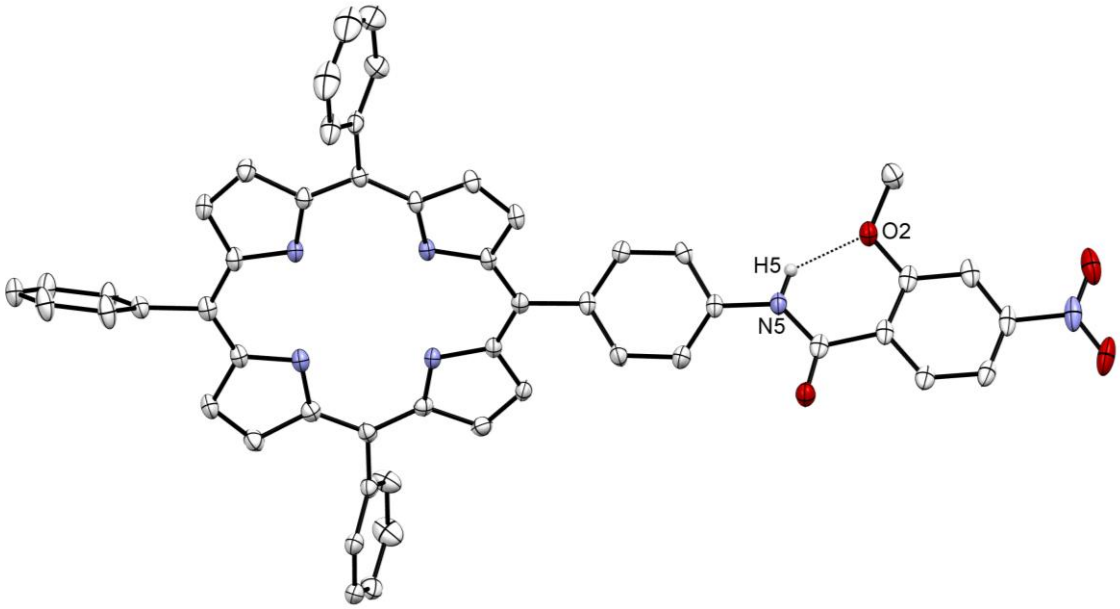

Figure S 16. X-ray crystal structure of 5-[4-[(2-methoxy-4-nitro-phenylcarbonyl)-amino]phenyl]-10,15,20-triphenyl porphyrin. Selected hydrogen atoms and solvent of crystallization omitted for clarity. H(5) was located. Thermal ellipsoids shown with probability of 50%. Selected bond length (Å): O(2)-N(5): 2.658(4).

Table S 1. Crystallographic data for **[Dyad 1 pic][PF_6] 2.5 CH_2Cl_2**

Identification code	rnp1309
Empirical formula	$C_{67.5}H_{49}Cl_5F_6N_8O_4PReZn$
Formula weight	1609.94
Temperature/K	110.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	12.9474(5)
b/Å	15.8804(5)
c/Å	17.3277(6)
α/°	98.752(3)
β/°	92.264(3)
γ/°	106.821(3)
Volume/$Å^3$	3357.4(2)
Z	2
$\rho_{calc}mg/mm^3$	1.592
m/mm^{-1}	2.452
F(000)	1602.0
Crystal size/mm^3	0.1612 × 0.091 × 0.0831
2Θ range for data collection	5.7 to 54.2°
Index ranges	$-16 \leq h \leq 16$, $-20 \leq k \leq 20$, $-22 \leq l \leq 18$
Reflections collected	25307
Independent reflections	14802[R(int) = 0.0307]
Data/restraints/parameters	14802/25/880
Goodness-of-fit on F^2	1.073
Final R indexes [I>=2σ (I)]	R_1 = 0.0659, wR_2 = 0.1868
Final R indexes [all data]	R_1 = 0.0809, wR_2 = 0.1986
Largest diff. peak/hole / e $Å^{-3}$	4.12/-1.78
CCDC number	1406001

Table S 2. Crystallographic data for 5-[4-[(2-methoxy-4-nitro-phenylcarbonyl)-amino]phenyl]-10,15,20-triphenyl porphyrin **0.595 CH_2Cl_2**

Empirical formula	$C_{52.59375}H_{37.1875}Cl_{1.1875}N_6O_4$
Formula weight	859.29
Temperature/K	110.00(10)
Crystal system	orthorhombic
Space group	Fddd
a/Å	23.5964(4)
b/Å	37.3470(6)
c/Å	40.0789(6)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/$Å^3$	35319.7(9)
Z	32
ρ_{calc}mg/mm^3	1.293
m/mm^{-1}	0.152
F(000)	14303.4
Crystal size/mm^3	0.1818 × 0.1617 × 0.1159
2Θ range for data collection	5.76 to 50.7°
Index ranges	$-25 \leq h \leq 28$, $-44 \leq k \leq 44$, $-45 \leq l \leq 48$
Reflections collected	26924
Independent reflections	8081[R(int) = 0.0340]
Data/restraints/parameters	8081/6/606
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0578, wR_2 = 0.1587
Final R indexes [all data]	R_1 = 0.0712, wR_2 = 0.1693
Largest diff. peak/hole / e $Å^{-3}$	0.85/-1.07
CCDC number	1406000

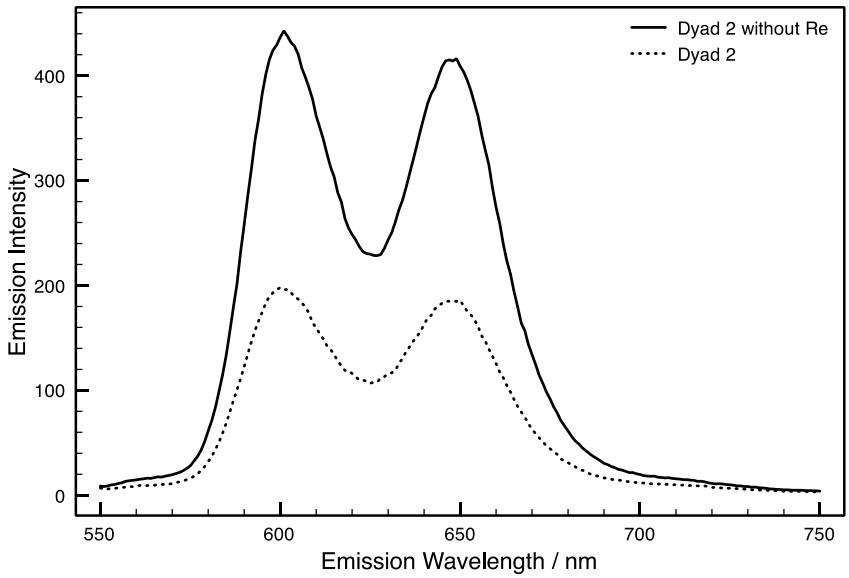

Figure S 17. Emission spectra of **[Dyad 2 pic]OTf** and the Zn porphyrin-bridge-bipyridine ligand of Dyad 2.

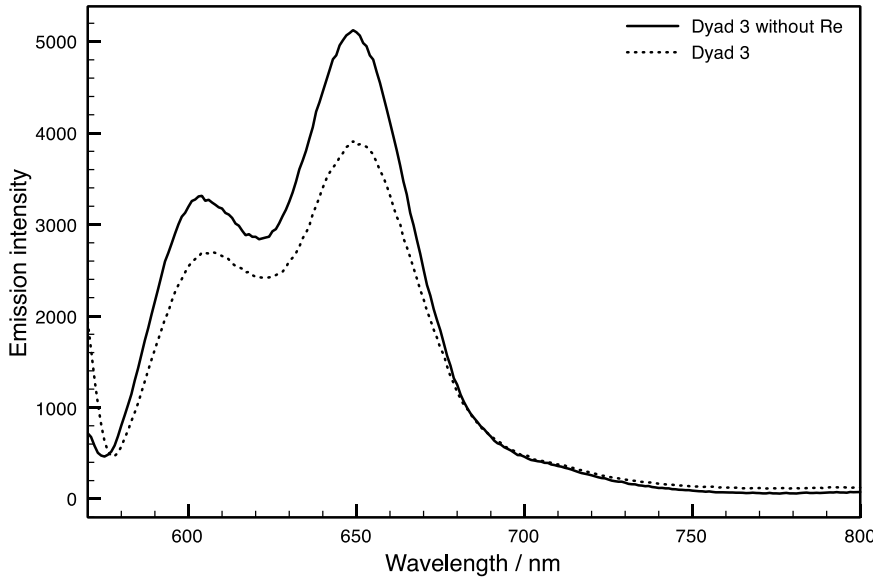

Figure S 18. Emission spectra of **[Dyad 3 pic]OTf** and the Zn porphyrin-bridge-bipyridine ligand of Dyad 3.

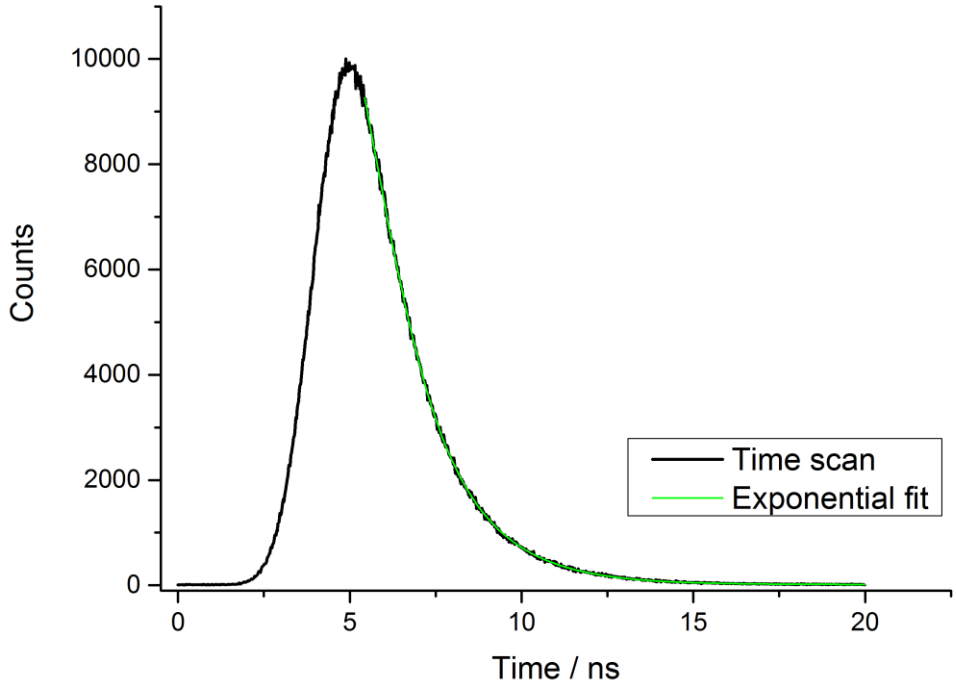

Figure S 19. Emission time scan (black) and fitting (green) for **[Dyad 3 pic]OTf**. λ_{ex} = 560 nm and λ_{em} = 605 nm.

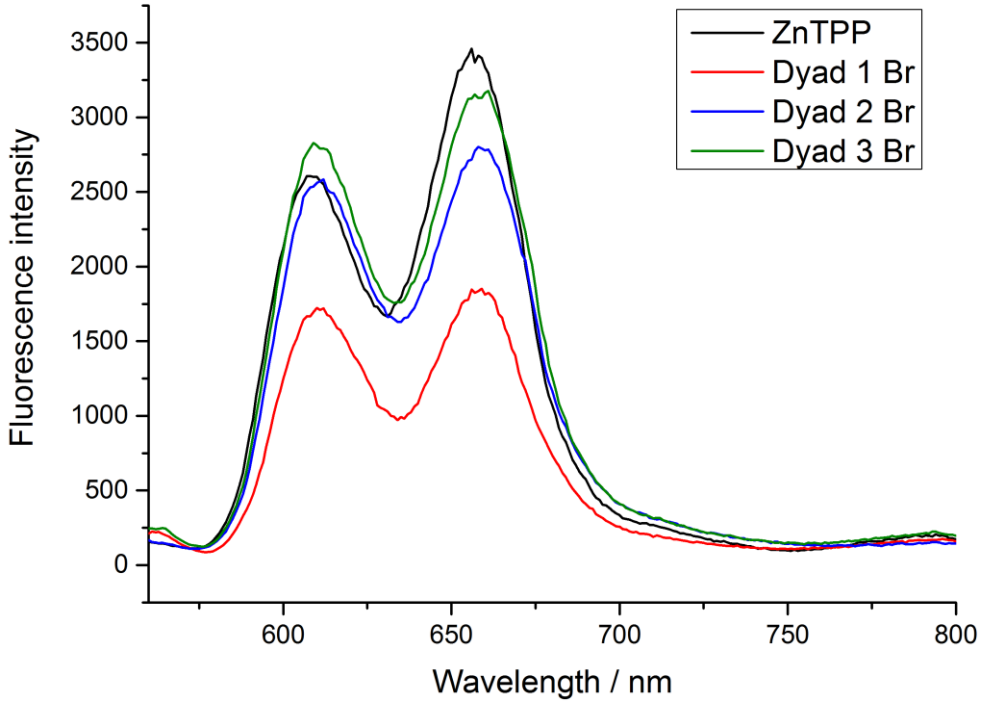

Figure S 20. Emission spectra of **ZnTPP**, **Dyad 1 Br**, **Dyad 2 Br** and **Dyad 3 Br** in THF.

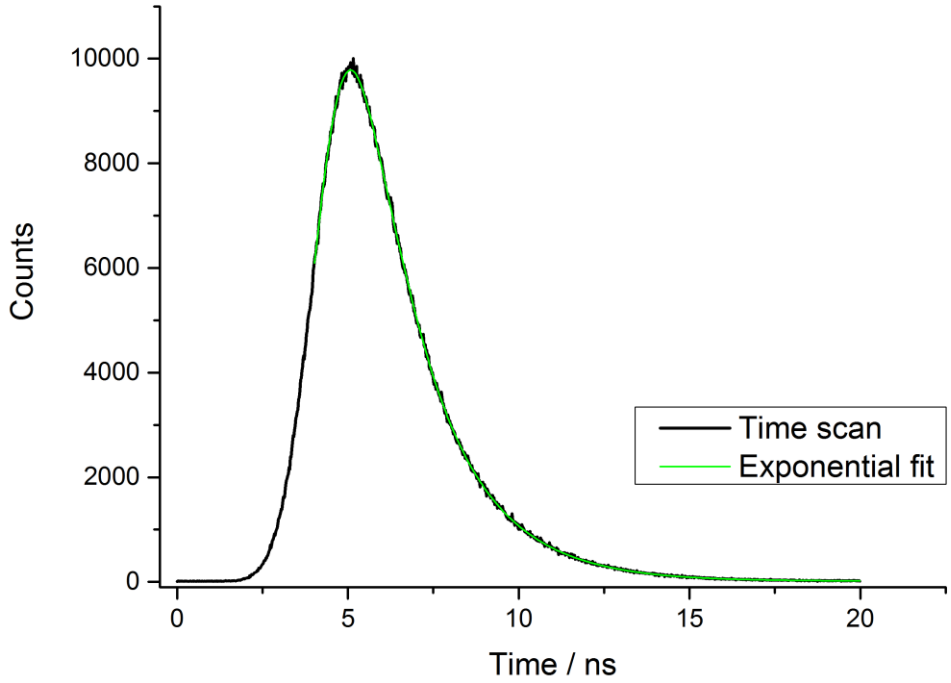

Figure S 21. Emission time scan (black) and fitting (green) for **Dyad 3 Br**. λ_{ex} = 560 nm and λ_{em} = 605 nm.

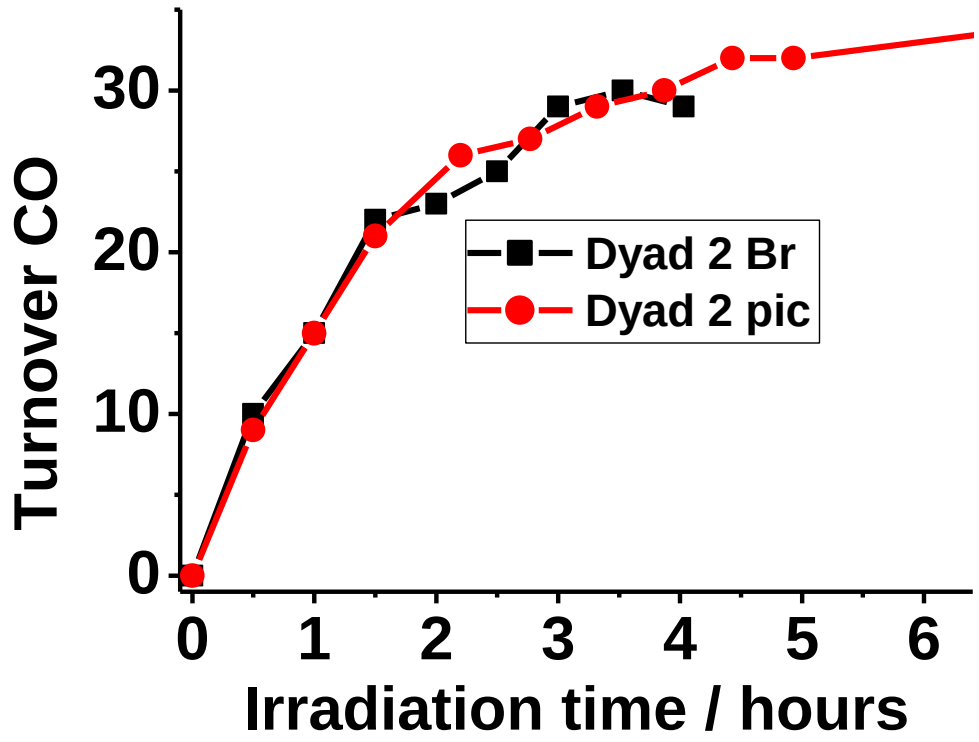

Figure S 22. TON_{CO} for **Dyad 2 Br** and **[Dyad 2 pic]OTf**. In DMF:TEOA 5:1 and with λ > 520 nm irradiation.

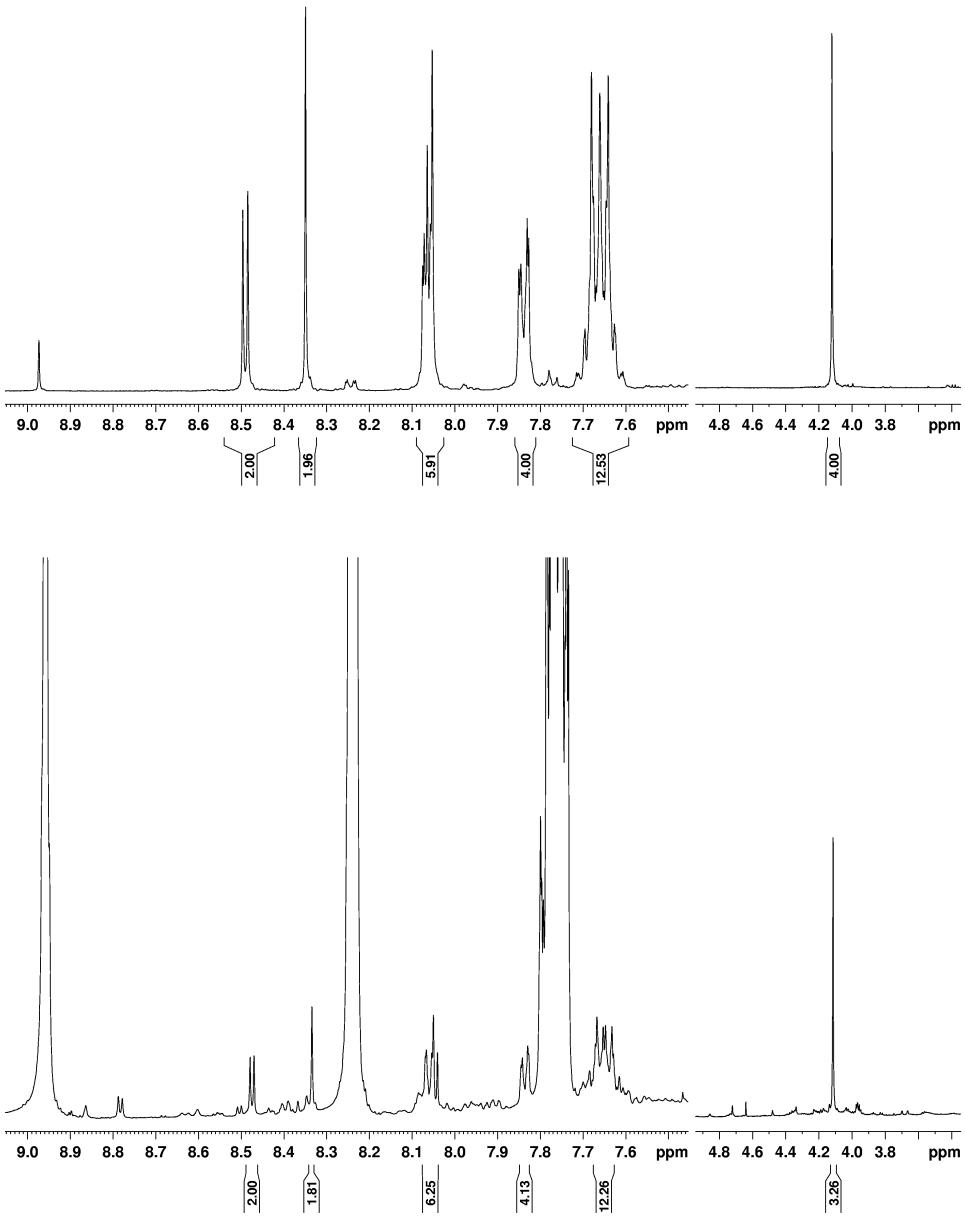

Figure S 23 ^{1}H NMR spectra. Above: authentic zinc tetraphenylchlorin, below: photoreaction mixture of ZnTPP in DMF:TEOA 5:1.

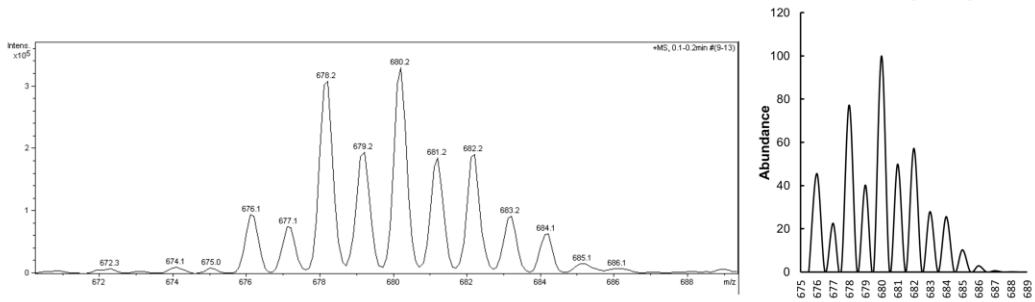

Figure S 24. Left: ESI-MS of ZnTPP in DMF/TEOA after irradiation with λ > 520 nm, right: calculated isotope pattern for ZnTPP, Zn chlorin and Zn isobacteriochlorin superimposed on top of one another in a 1:1:1 ratio.

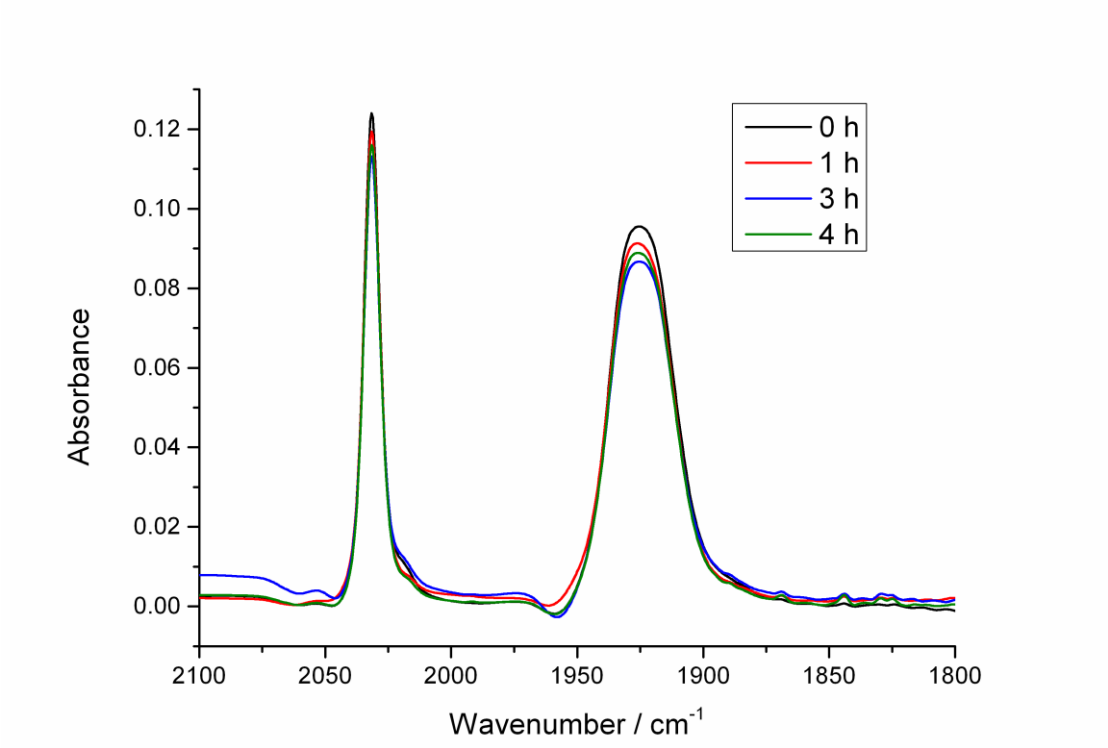

Figure S 25. IR spectra of **[Dyad 2 pic]OTf** following dissolution in DMF at times given.

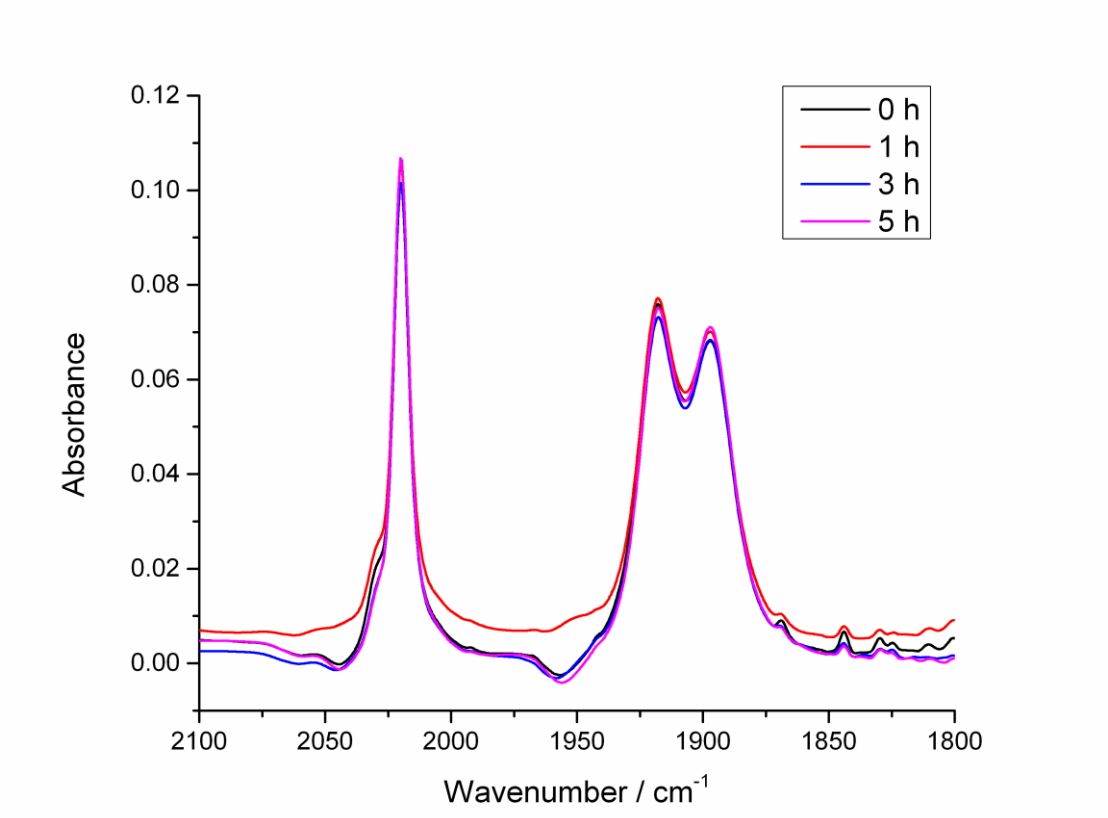

Figure S 26. IR spectra of **Dyad 2 Br** following dissolution in DMF at times given.

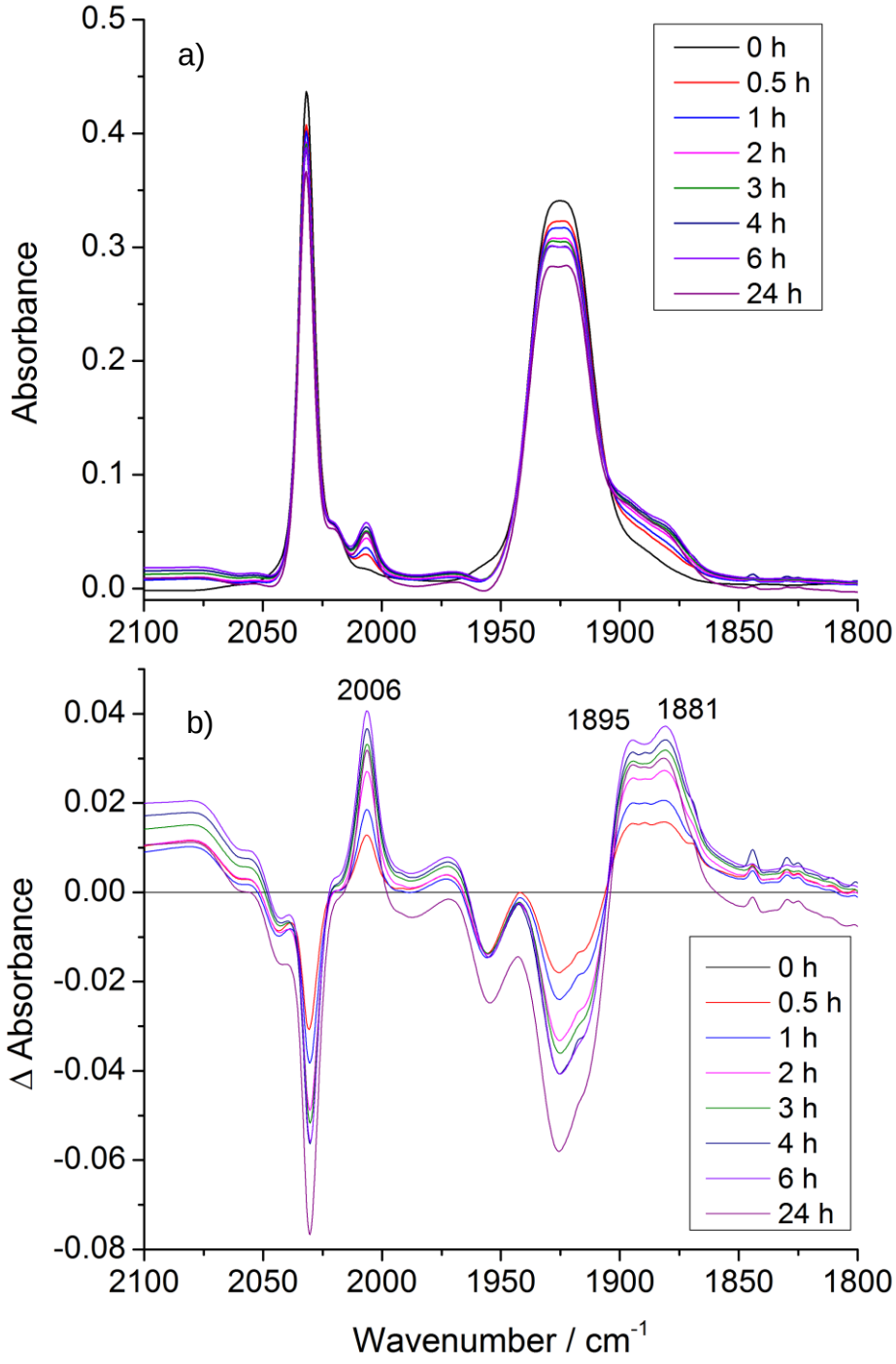

Figure S 27. IR spectra of **[Dyad 2 pic]OTf** in DMF after addition of TEOA (DMF:TEOA 5:1): a) absorption spectra at times after addition of TEOA, b) difference spectra at same times.

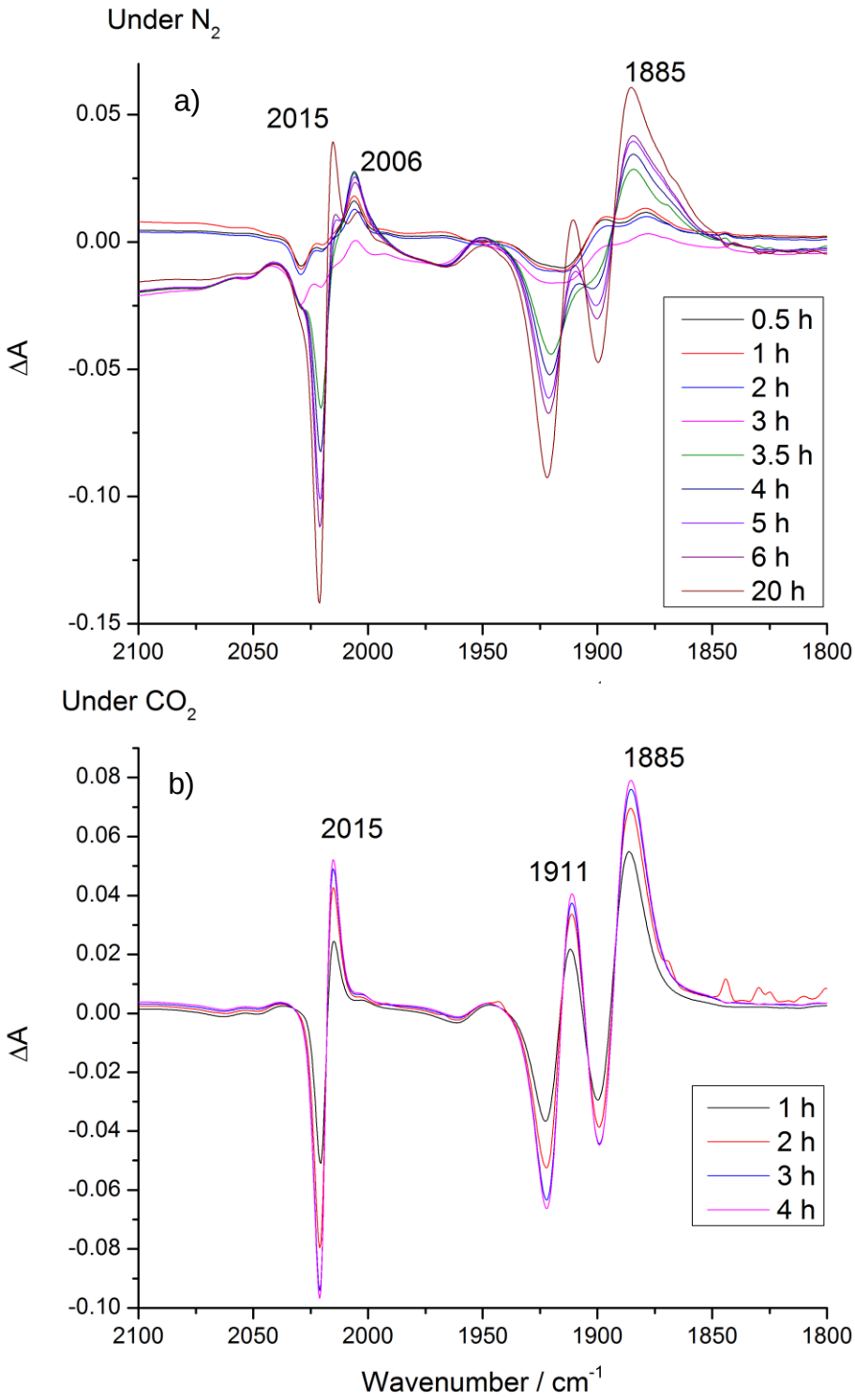

Figure S 28. IR difference spectra of **Dyad 2 Br** in DMF after addition of TEOA (DMF:TEOA 5:1) and with λ > 520 nm irradiation relative to before addition of TEOA: a) under N_2, b) same sample following bubbling of CO_2.

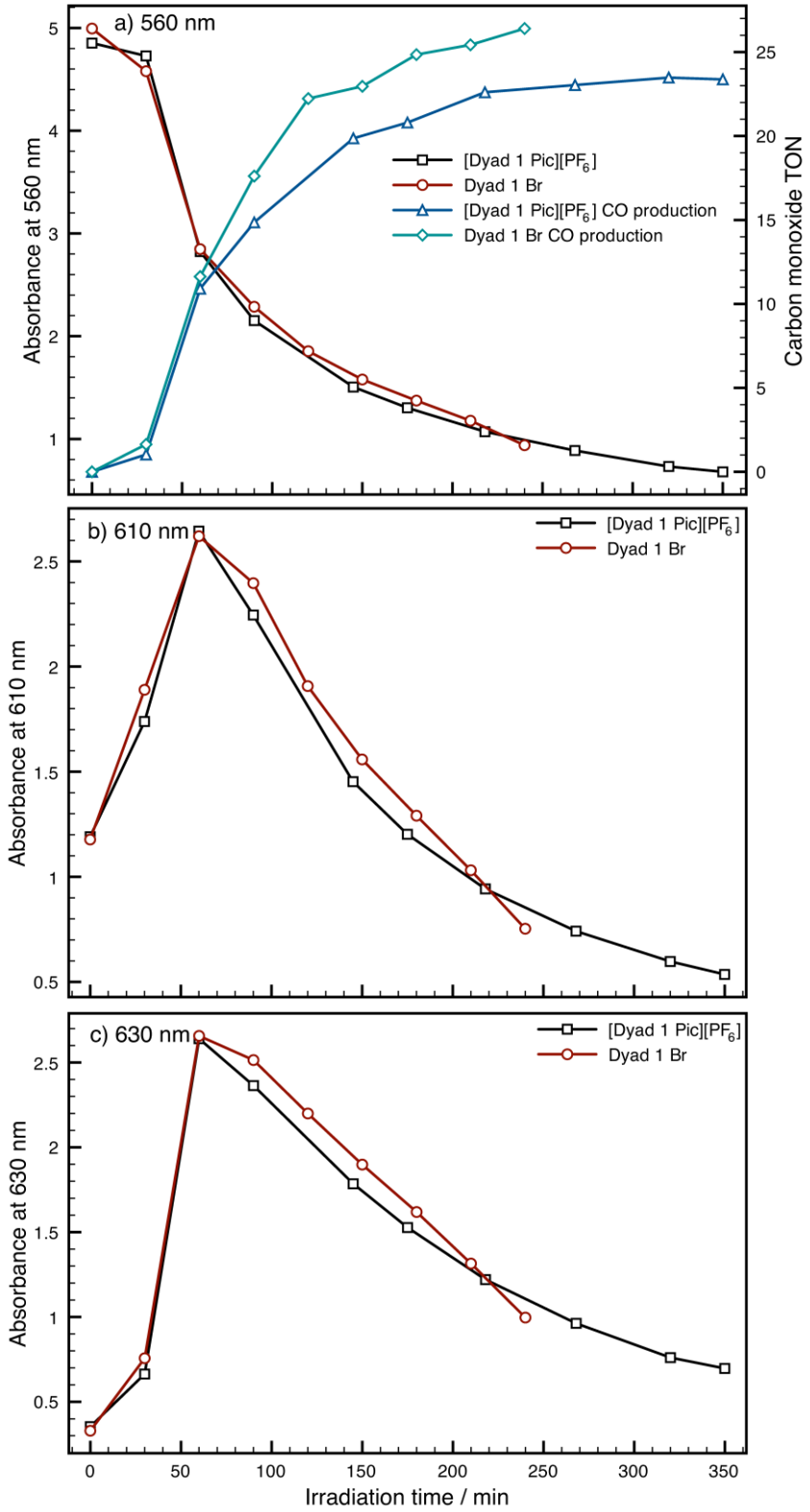

Figure S 29. Absorbance changes in the UV/vis spectra of **Dyad 1 Br** and **[Dyad 1 pic]PF_6** during CO_2 reduction: a) changes in signal intensity at 560 nm and turnovers of CO, b) changes in signal intensity at 610 nm, c) changes in signal intensity at 630 nm.