

Electronic Supplementary Information

Porphyrin-Cobaloxime Dyads for Photoinduced Hydrogen Production: Investigation of the Primary Photochemical Process

*Mirco Natali,^{*a,b} Michele Orlandi,^{a,b} Claudio Chiorboli,^c Elisabetta Iengo,^{*d} Valerio Bertolasi,^a
and Franco Scandola^{*a,b}*

(a) Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Ferrara, via
Fossato di Mortara 17-19, 44121 Ferrara, Italy. E-mail: mirco.natali@unife.it, snf@unife.it.

(b) Centro Interuniversitario per la Conversione Chimica dell'Energia Solare, sezione di Ferrara, via
L. Borsari 46, 44121 Ferrara, Italy.

(c) ISOF-CNR, sezione di Ferrara, via L. Borsari 46, 44121 Ferrara, Italy.

(d) Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, via L.
Giorgeri 1, 34127 Trieste, Italy. E-mail: eiengo@units.it

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Materials and Methods

Materials. Solvents for spectroscopic, photophysical and photolysis measurements were of spectroscopic grade, all the other reagents were of reagent grade quality, and used as received.

NMR. ^1H spectra were recorded at 400 MHz on a *Bruker Avance 400 QNP* and at 500 MHz on a *Bruker Avance 500*. All spectra were run at room temperature (298 K) in pyridine- d_5 , acetonitrile- d_3 , dichloromethane- d_2 and chloroform- d_1 . Proton peak positions were referenced to the peak of residual non deuterated solvent.

X-Ray crystallography. Single crystal data of the complex **1** were collected on a *Nonius Kappa CCD* diffractometer using graphite monochromated Mo K α radiation ($\lambda=0.7107\text{\AA}$) at 295 K. Data sets were integrated with the *Denzo SMN* package^[S1] and corrected for Lorentz-polarization and absorption effects.^[S2] The structure was solved by direct methods (SIR97)^[S3] and refined by full-matrix least-squares methods with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms. The Cl atoms of the disordered molecule of CHCl_3 were refined over two sites. To increase stability of refinement, a system of restraints to the CHCl_3 geometry was employed.

Because of the presence of an ill-defined region of residual density, the refinement was far from satisfactory. For this reason the program *SQUEEZE* was used to cancel out the effects of the disordered solvent. *SQUEEZE* is part of the *PLATON* program system^[S4] and attempts to remove mathematically the effects of disordered solvent.

All calculations were performed using *SHELXL-97*^[S5] implemented in the *WINGX* system of programs^[S6].

Electrochemical Measurements. Cyclic Voltammetry (CV) measurements were carried out with a PC-interfaced *Eco Chemie Autolab/Pgstat 30* Potentiostat. Argon-purged 10^{-4} M sample solutions in THF, containing 0.1 M (TBA)PF $_6$ (Fluka, electrochemical grade, 99%; dried in an

oven), were used. A conventional three-electrode cell assembly was adopted: a saturated calomel electrode (*SCE Amel*) and a platinum electrode, both separated from the test solution by a frit, were used as reference and counter electrodes, respectively; a glassy carbon electrode was used as the working electrode.

Steady-state Absorption/Emission Measurements. UV-Vis absorption spectra were recorded on a *Jasco V-570 UV/Vis/NIR* spectrophotometer. Emission spectra were taken on a *Horiba-Jobin Yvon Fluoromax-2* spectrofluorimeter, equipped with a *Hamamatsu R3896* tube.

Time-Correlated Single Photon Counting (TCSPC). Fluorescence lifetimes were measured using a TCSPC apparatus (*PicoQuant Picoharp 300*) equipped with subnanosecond LED sources (280, 380, 460, and 600 nm, 500-700 ps pulsewidth) powered by a *PicoQuant PDL 800-B* variable (2.5-40 MHz) pulsed power supply. The decays were analyzed by means of *PicoQuant FluoFit* Global Fluorescence Decay Analysis Software.

Ultrafast Spectroscopy (UFS). Femtosecond time-resolved experiments were performed using a pump-probe setup based on the *Spectra-Physics Hurricane* Ti:sapphire laser source and the Ultrafast Systems Helios spectrometer.^[S7] The 530 and 550-nm pump pulses were generated with a *Spectra Physics 800 OPA*. Probe pulses were obtained by continuum generation on a sapphire plate (useful spectral range: 450-800 nm). Effective time resolution *ca.* 300 fs, temporal chirp over the white-light 450-750 nm range *ca.* 200 fs, temporal window of the optical delay stage 0-2000 ps. The time-resolved spectral data were analyzed with the *Ultrafast Systems Surface Explorer Pro* software.

Synthesis

Molecular precursors

5-(4'-pyridyl)-10,15,20-triphenylporphyrin. 5-(4'-pyridyl)-10,15,20-triphenylporphyrin was synthesized and purified according to literature methods.^[S8]

[5-(4'-pyridyl)-10,15,20-triphenylporphyrinato] zinc(II). A concentrated CH₂Cl₂ solution of 5-(4'-pyridyl)-10,15,20-triphenylporphyrin was treated overnight with an 8-fold molar excess of Zn(CH₃COO)₂ dissolved in the minimum amount of MeOH. The solution was dried in vacuo and the obtained solid dissolved in CH₂Cl₂. The product was precipitated by addition of *n*-hexane, removed by filtration, washed thoroughly with cold methanol and diethyl ether and vacuumdried (Yield > 85%). ¹H NMR (CDCl₃), δ_H: 8.90 (2H, d, β₄), 8.85 (2H, d, β₃), 8.55 (2H, d, β₂), 8.20 (2H, d, oH'), 8.10 (4H, d, oH), 7.75 (3H, m, mH'+pH'), 7.68 (6H, m, mH+pH), 7.45 (2H, d, β₁), 6.25 (2H, br s, py_{Hb}), 3.45 (2H, br s, py_{Ha}).

[5-(4'-pyridyl)-10,15,20-(3,5-di-*tert*-butyl)-triphenylporphyrinato-hydroxo]

aluminum(III).^[S9] 300 mg (2.82 mmol) of 5-(4'-pyridyl)-10,15,20-(3,5-di-*tert*-butyl)-triphenylporphyrin were dissolved in 100 ml of dry toluene and 0.2 ml of trimethylaluminium (2.0 M in toluene, 5.6 mmol) were added under N₂ atmosphere. The solution was stirred at room T, under N₂ atmosphere, for 4 hr, at which time 5 ml of H₂O were added and stirring was continued overnight. The toluene was removed and the violet solid thus formed was redissolved in CH₂Cl₂. The solution was filtered dried over Na₂SO₄ and passed over a column of alumina to give 265 mg of product (85%). ¹H NMR (pyridine-*d*₅), δ_H: 9.28 (6H, m, β₄+β₃+β₂), 9.12 (4H, m, β₁+py_{Ha}), 8.2 (6H, br d, oH+oH'), 8.15 (2H, d, py_{Hb}), 7.84 (3H, d, br, pH+pH'), 1.54 (s, *t*Bu), 1.52 (s, *t*Bu).

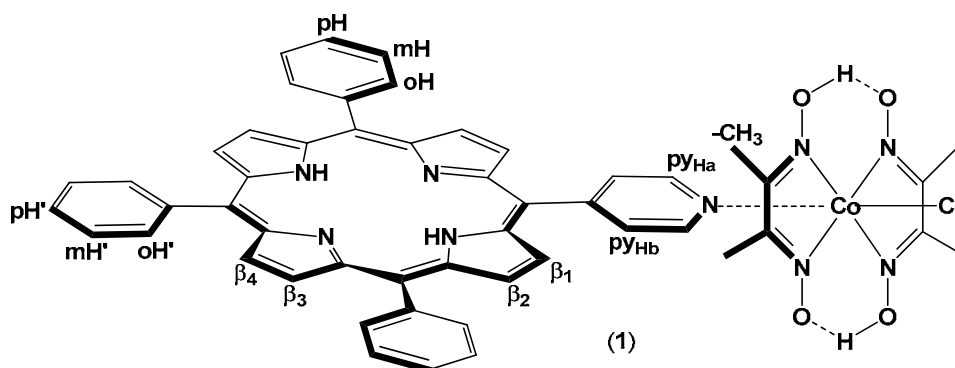
Chloro(acquo)bis(dimethylglyoximate) cobalt(III). Co(dmGH)₂Cl(H₂O) was synthesized according to literature procedures.^[S10] 1.10 g of CoCl₂·6H₂O (5 mmol) and 1.18 g of dmGH₂ (dimethylglyoxime, 11 mmol) were dissolved in 50 ml of 95% ethanol, and heated at 70°C. 5 ml of

a 1 M NaOH solution (5 mmol) were then added to the whole mixture and the solution was stirred for 1 hr at 70°C. After cooling at room temperature, a stream of air was blown through the solution for 30 min. The solution was filtered to remove side-reaction products and concentrated under vacuum to allow precipitation. The so obtained brown solid was collected by filtration on a Büchner funnel and washed with 5 ml water and then with 10 ml diethyl ether. The solid was then dried at room temperature to yield 590 mg of product (35%). ^1H NMR (acetonitrile- d_3), δ_{H} : 18.40 (2H, br s, OHO), 2.45 (12H, s, CH_3).

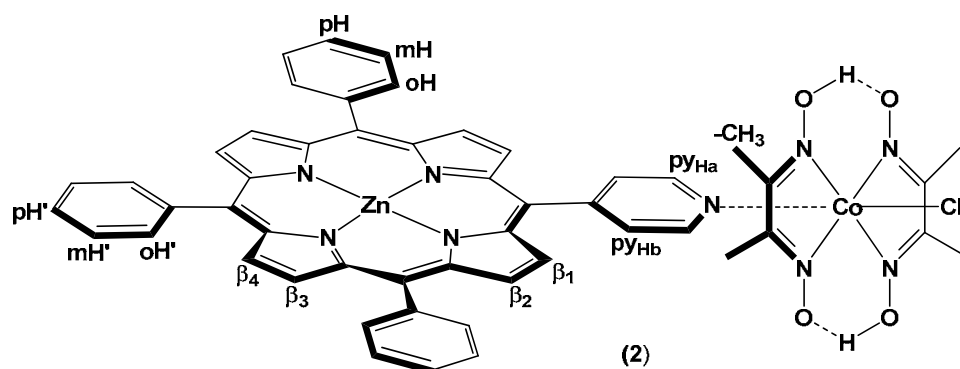
Molecular dyads 1-3

{5-(4'-pyridyl)-10,15,20-triphenylporphyrin}chloro bis(dimethylglyoximate) cobalt(III) (1).

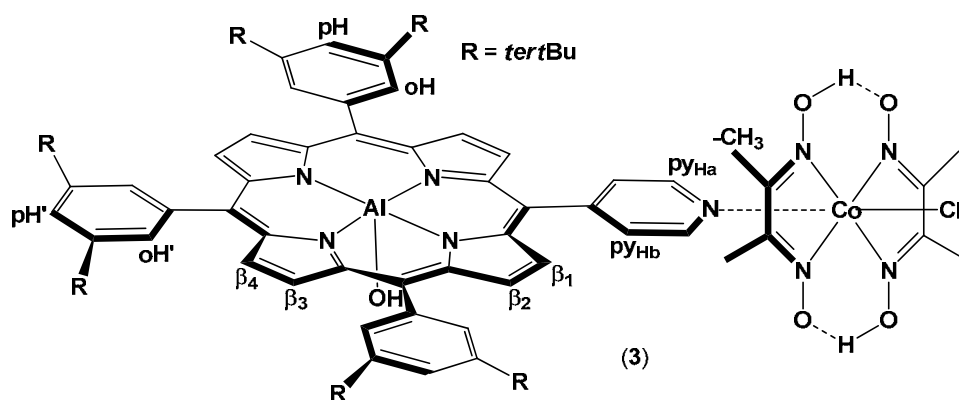
49.2 mg (0.08 mmol) of 5-(4'-pyridyl)-10,15,20-triphenylporphyrin were dissolved in 400 ml of a 1/5 $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ mixture and 101.2 mg (0.32 mmol) of $\text{Co}(\text{dmgH})_2\text{Cl}(\text{H}_2\text{O})$ were added to the solution under continuous stirring. The reaction mixture was left stirring for 1 hr at room temperature, and then concentrated to allow precipitation; the violet solid was collected by filtration on a Büchner funnel and washed with 10 ml diethyl ether to yield 55.2 mg of **1** (73%). ^1H NMR (CD_2Cl_2), δ_{H} : 18.65 (2H, br s, OHO), 8.93 (6H, m, $\text{py}_{\text{Ha}} + \beta_3 + \beta_4$), 8.70 (2H, d, β_2), 8.66 (2H, d, β_1), 8.24 (6H, m, $\text{oH} + \text{oH}'$), 8.16 (2H, d, py_{Hb}), 7.84 (9H, m, $\text{mH} + \text{mH}' / \text{pH} + \text{pH}'$), 2.60 (12H, s, CH_3), -2.85 (2H, s, NH).



{[5-(4'-pyridyl)-10,15,20-triphenylporphyrinato] zinc(II)} chloro bis(dimethylglyoximate) cobalt(III) (2). 22.3 mg (0.03 mmol) of [5-(4'-pyridyl)-10,15,20-triphenylporphyrinato] zinc(II) were dissolved in 190 ml 1/5 CH₃CN/CH₂Cl₂ mixture and 41.5 mg (0.12 mmol) of Co(dm₂H)₂Cl(H₂O) were added to the solution under continuous stirring. The reaction mixture was left stirring for 1 hr at room temperature, and then concentrated to allow precipitation. The violet solid was collected by filtration on a Büchner funnel and washed with 10 ml diethyl ether to yield 23.4 mg of **2** (71%). ¹H NMR (CD₂Cl₂), δ_H: 18.65 (2H, br s, OHO), 9.00 (6H, m, β₂+ β₃+ β₄), 8.78 (2H, d, β₁), 8.63 (2H, d, py_{Ha}), 8.23 (6H, m, oH+oH'), 8.16 (2H, d, py_{Hb}), 7.82 (9H, m, mH+mH'/pH+pH'), 2.60 (12H, s, CH₃).



{[5-(4'-pyridyl)-10,15,20-(3,5-di-*tert*-butyl)-triphenylporphyrinato-hydroxo] aluminum(III)}chloro bis(dimethylglyoximate) cobalt(III) (3). 30 mg (0.03 mmol) of [5-(4'-pyridyl)-10,15,20-(3,5-di-*tert*-butyl)-triphenylporphyrinato-hydroxo] aluminum(III) were dissolved in 190 ml 1/5 CH₃CN/CH₂Cl₂ mixture and 41.1 mg (0.12 mmol) of Co(dm₂H)₂Cl(H₂O) were added to the solution under continuous stirring. The reaction mixture was left stirring for 1 hr at room temperature, and was then concentrated to allow precipitation. The violet solid was collected by filtration on a Büchner funnel and washed with 10 ml diethyl ether to yield 21.7 mg of **3** (55%). ¹H NMR (CD₂Cl₂), δ_H: 18.4 (2H, br s, OHO), 9.00 (8H, m, β₂+ β₃+ β₄+ py_{Ha}), 8.69 (2H, d, β₁), 8.10 (8H, m, oH+oH'+py_{Hb}), 7.78 (3H, m, pH+pH'), 2.45 (12H, s, CH₃), 1.65 (m, *t*Bu).



Molecular models 4-6

5,10,15,20-tetraphenylporphyrin (4), [5,10,15,20-tetraphenylporphyrinato] zinc(II) (5), and 5,10,15,20-(3,5-di-*tert*-butyl)-tetraphenylporphyrinato-hydroxo} aluminum(III) (6) were prepared with the same experimental procedures reported before for the monopyridyl porphyrin analogues (vide supra).

Chloro(4-ethylpyridine)bis(dimethylglyoximate) cobalt(III). Co(dmgh)₂Cl(EtPy) was synthesized according to literature procedures.^[S10]

X-ray molecular structure of dyad 1 and crystallographic data

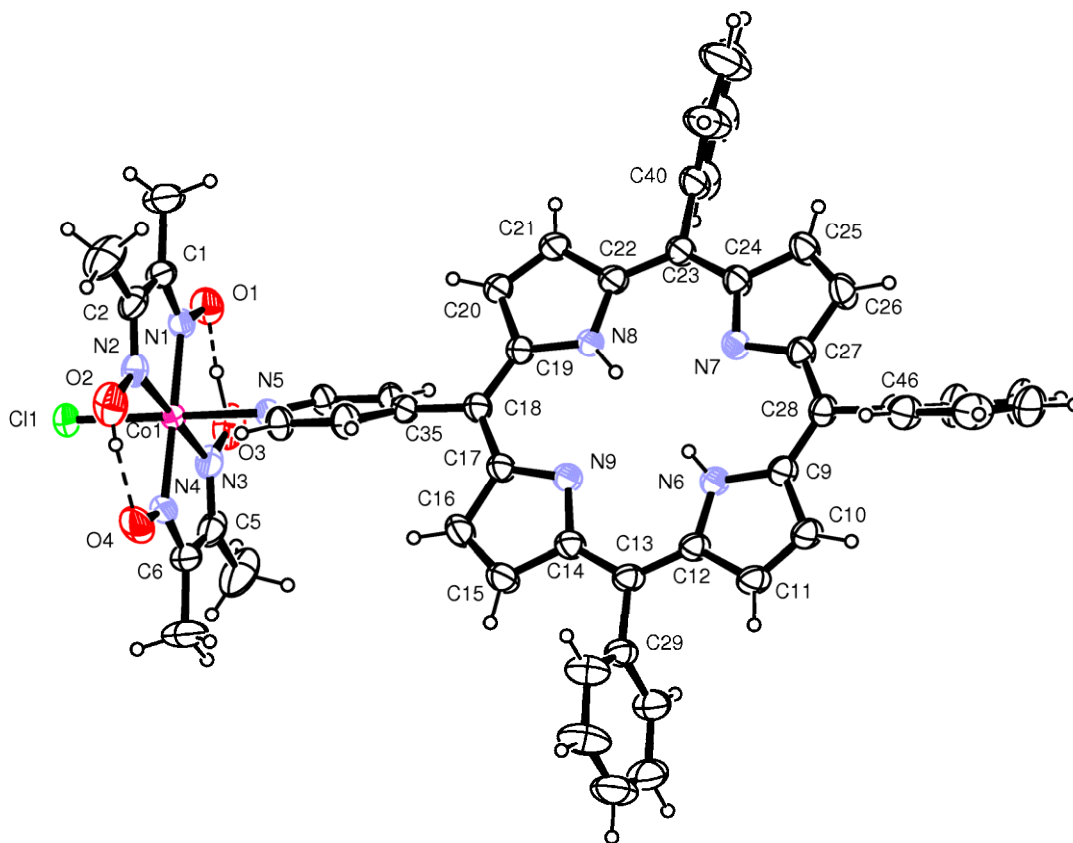


Figure S1. ORTEP^[S11] diagram of dyad 1. Thermal ellipsoids are drawn at the 30% probability level.

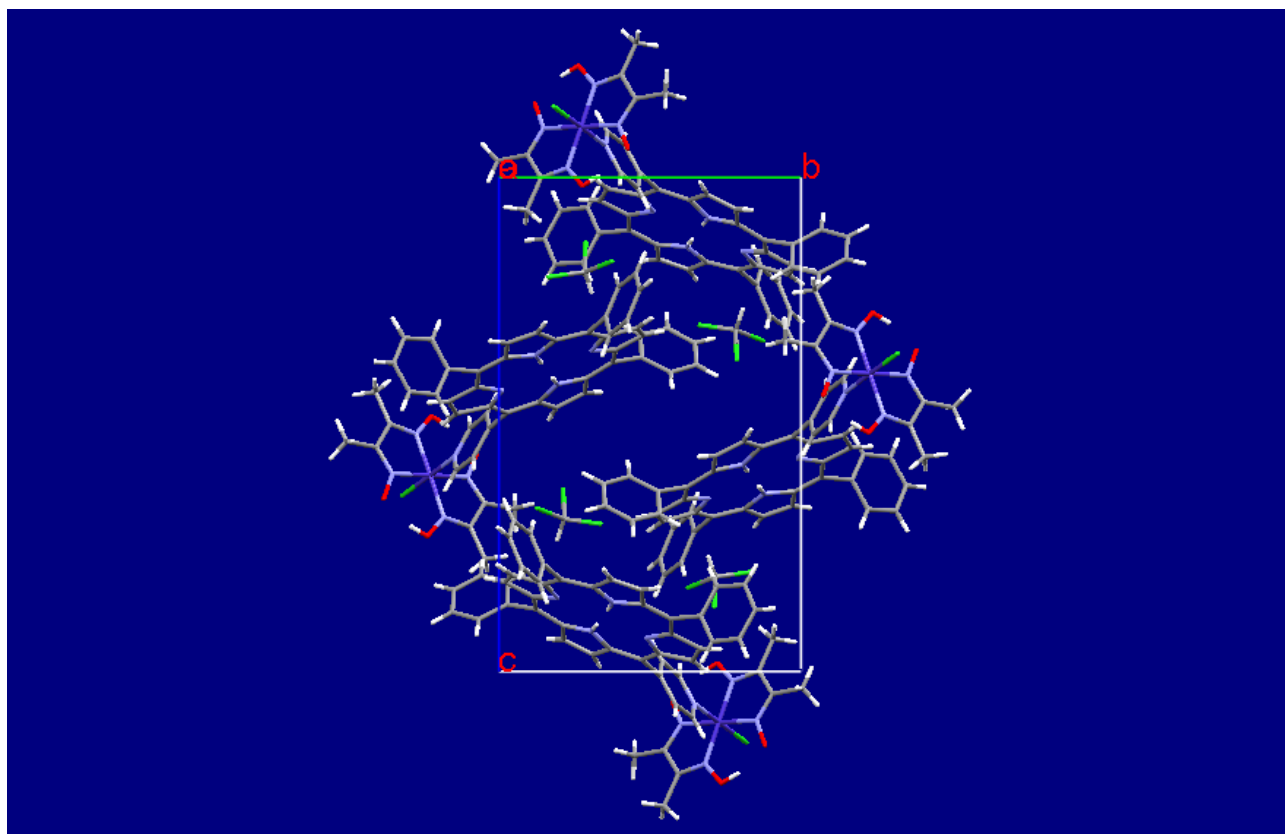


Figure S2. Crystal packing of dyad 1.

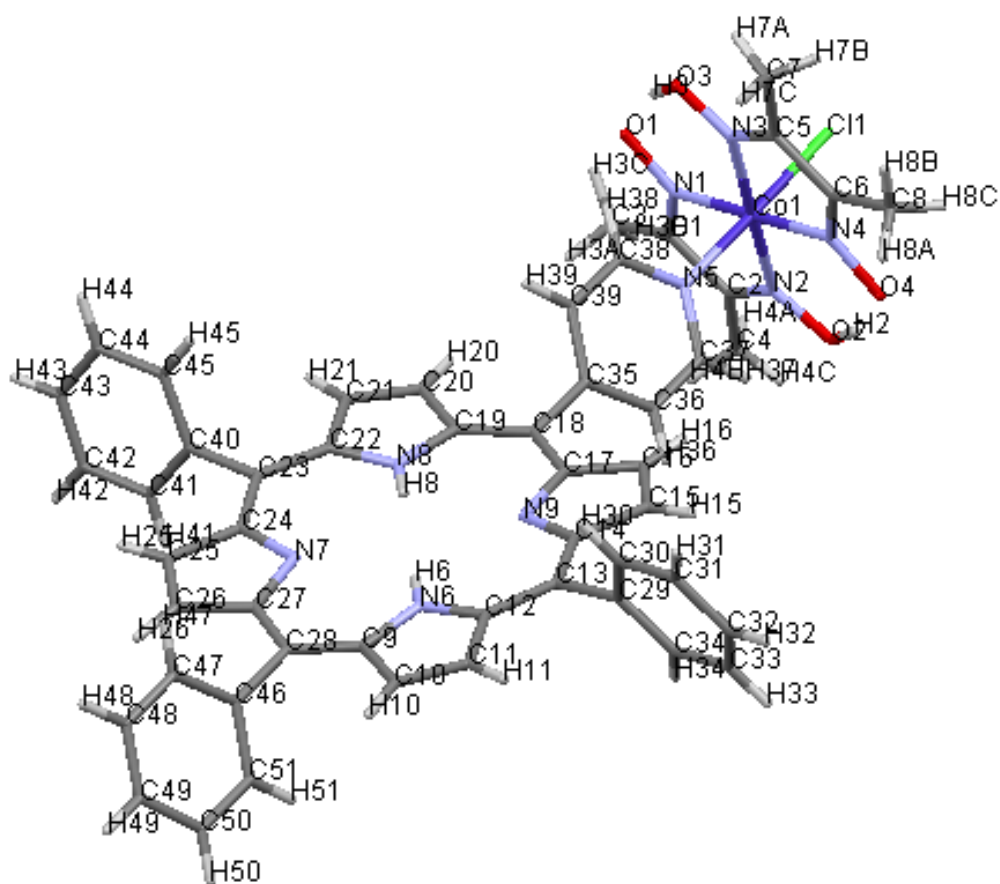


Figure S3. Atom labeling on the molecular structure of dyad 1.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{51}H_{43}ClCoN_9O_4 \cdot CHCl_3$	
Formula weight	1059.69	
Temperature	295 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 20.2161(3)$ Å	$\alpha = 90^\circ$
	$b = 12.5775(2)$ Å	$\beta = 99.3737(6)^\circ$
	$c = 20.8200(4)$ Å	$\gamma = 90^\circ$
Volume	$5223.2(2)$ Å ³	
Z	4	
Crystal size	0.17 x 0.29 x 0.36 mm ³	
Theta range for data collection	3.58 to 26.00°	
Index ranges	-24 ≤ h ≤ 24, -14 ≤ k ≤ 15, -25 ≤ l ≤ 25	
Reflections collected	19016	
Independent reflections	10202 [R(int) = 0.0231]	
Completeness to theta = 26.00°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.895 and 0.807	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	10202 / 15 / 658	
Goodness-of-fit on F ²	1.104	
Final R indices [I > 2σ(I)]	R1 = 0.0631, wR2 = 0.1899	
R indices (all data)	R1 = 0.0825, wR2 = 0.2067	
Largest diff. peak and hole	0.620 and -0.612 e.Å ⁻³	
CCDC Deposition No.	944790	

Table 2. Bond distances and angles (\AA , $^\circ$) in **1**, see Figure S3 for atom labels

Co1—N1	1.883 (2)	C20—C21	1.355 (5)
Co1—N4	1.886 (3)	C20—H20	0.9300
Co1—N3	1.889 (3)	C21—C22	1.430 (4)
Co1—N2	1.893 (3)	C21—H21	0.9300
Co1—N5	1.976 (2)	C22—C23	1.392 (4)
Co1—Cl1	2.2422 (8)	C23—C24	1.416 (4)
N1—C1	1.291 (4)	C23—C40	1.499 (5)
N1—O1	1.332 (3)	C24—C25	1.429 (4)
N2—C2	1.296 (4)	C25—C26	1.326 (5)
N2—O2	1.350 (3)	C25—H25	0.9300
O2—H2	0.8200	C26—C27	1.450 (5)
C1—C2	1.457 (5)	C26—H26	0.9300
C1—C3	1.487 (5)	C27—C28	1.389 (4)
C2—C4	1.488 (5)	C28—C46	1.490 (4)
C3—H3A	0.9600	C29—C34	1.366 (6)
C3—H3B	0.9600	C29—C30	1.394 (5)
C3—H3C	0.9600	C30—C31	1.423 (7)
C4—H4A	0.9600	C30—H30	0.9300
C4—H4B	0.9600	C31—C32	1.319 (8)
C4—H4C	0.9600	C31—H31	0.9300
N3—C5	1.300 (5)	C32—C33	1.359 (8)
N3—O3	1.329 (4)	C32—H32	0.9300
O3—H3	0.8200	C33—C34	1.366 (6)
N4—C6	1.296 (5)	C33—H33	0.9300
N4—O4	1.350 (4)	C34—H34	0.9300
C5—C6	1.444 (7)	C35—C39	1.387 (4)
C5—C7	1.490 (6)	C35—C36	1.393 (4)
C6—C8	1.514 (6)	C36—C37	1.378 (4)
C7—H7A	0.9600	C36—H36	0.9300
C7—H7B	0.9600	C37—H37	0.9300
C7—H7C	0.9600	C38—C39	1.369 (4)
C8—H8A	0.9600	C38—H38	0.9300
C8—H8B	0.9600	C39—H39	0.9300
C8—H8C	0.9600	C40—C41	1.360 (7)
N5—C37	1.332 (4)	C40—C45	1.399 (7)
N5—C38	1.340 (4)	C41—C42	1.390 (8)
N6—C9	1.365 (4)	C41—H41	0.9300
N6—C12	1.368 (4)	C42—C43	1.350 (11)
N6—H6	0.8600	C42—H42	0.9300
N7—C24	1.374 (4)	C43—C44	1.307 (11)
N7—C27	1.387 (4)	C43—H43	0.9300
N8—C19	1.368 (4)	C44—C45	1.399 (7)
N8—C22	1.378 (4)	C44—H44	0.9300
N8—H8	0.8600	C45—H45	0.9300
N9—C17	1.372 (4)	C46—C47	1.383 (5)
N9—C14	1.380 (4)	C46—C51	1.392 (5)

C9—C28	1.406 (5)	C47—C48	1.370 (6)
C9—C10	1.430 (4)	C47—H47	0.9300
C10—C11	1.340 (5)	C48—C49	1.336 (7)
C10—H10	0.9300	C48—H48	0.9300
C11—C12	1.424 (4)	C49—C50	1.374 (7)
C11—H11	0.9300	C49—H49	0.9300
C12—C13	1.405 (4)	C50—C51	1.412 (6)
C13—C14	1.395 (4)	C50—H50	0.9300
C13—C29	1.503 (4)	C51—H51	0.9300
C14—C15	1.427 (5)	C1A—C11B	1.606 (9)
C15—C16	1.351 (5)	C1A—C12A	1.625 (6)
C15—H15	0.9300	C1A—C13B	1.662 (13)
C16—C17	1.448 (4)	C1A—C12B	1.681 (13)
C16—H16	0.9300	C1A—C13A	1.697 (7)
C17—C18	1.403 (4)	C1A—C11A	1.720 (7)
C18—C19	1.412 (4)	C1A—H1A	0.9800
C18—C35	1.487 (4)	C12B—C13B	2.47 (3)
C19—C20	1.432 (4)		
N1—Co1—N4	179.30 (11)	C22—C21—H21	125.8
N1—Co1—N3	98.08 (12)	N8—C22—C23	127.1 (3)
N4—Co1—N3	82.31 (14)	N8—C22—C21	107.1 (3)
N1—Co1—N2	81.32 (11)	C23—C22—C21	125.7 (3)
N4—Co1—N2	98.28 (13)	C22—C23—C24	126.0 (3)
N3—Co1—N2	178.35 (11)	C22—C23—C40	118.1 (3)
N1—Co1—N5	90.92 (10)	C24—C23—C40	116.0 (3)
N4—Co1—N5	89.66 (10)	N7—C24—C23	124.8 (3)
N3—Co1—N5	90.77 (10)	N7—C24—C25	110.0 (3)
N2—Co1—N5	90.78 (10)	C23—C24—C25	125.2 (3)
N1—Co1—C11	88.48 (7)	C26—C25—C24	107.9 (3)
N4—Co1—C11	90.95 (8)	C26—C25—H25	126.1
N3—Co1—C11	88.19 (8)	C24—C25—H25	126.1
N2—Co1—C11	90.25 (8)	C25—C26—C27	107.5 (3)
N5—Co1—C11	178.71 (7)	C25—C26—H26	126.2
C1—N1—O1	119.9 (3)	C27—C26—H26	126.2
C1—N1—Co1	117.0 (2)	N7—C27—C28	125.5 (3)
O1—N1—Co1	123.1 (2)	N7—C27—C26	108.8 (3)
C2—N2—O2	121.1 (3)	C28—C27—C26	125.7 (3)
C2—N2—Co1	116.0 (2)	C27—C28—C9	125.0 (3)
O2—N2—Co1	123.0 (2)	C27—C28—C46	118.7 (3)
N2—O2—H2	109.5	C9—C28—C46	116.3 (3)
N1—C1—C2	112.4 (3)	C34—C29—C30	119.0 (3)
N1—C1—C3	123.7 (4)	C34—C29—C13	121.4 (3)
C2—C1—C3	123.9 (3)	C30—C29—C13	119.6 (4)
N2—C2—C1	113.2 (3)	C29—C30—C31	117.8 (5)
N2—C2—C4	123.9 (4)	C29—C30—H30	121.1
C1—C2—C4	122.8 (4)	C31—C30—H30	121.1
C1—C3—H3A	109.5	C32—C31—C30	121.2 (5)

C1—C3—H3B	109.5	C32—C31—H31	119.4
H3A—C3—H3B	109.5	C30—C31—H31	119.4
C1—C3—H3C	109.5	C31—C32—C33	120.6 (4)
H3A—C3—H3C	109.5	C31—C32—H32	119.7
H3B—C3—H3C	109.5	C33—C32—H32	119.7
C2—C4—H4A	109.5	C32—C33—C34	120.3 (5)
C2—C4—H4B	109.5	C32—C33—H33	119.8
H4A—C4—H4B	109.5	C34—C33—H33	119.8
C2—C4—H4C	109.5	C29—C34—C33	121.1 (4)
H4A—C4—H4C	109.5	C29—C34—H34	119.4
H4B—C4—H4C	109.5	C33—C34—H34	119.4
C5—N3—O3	121.7 (3)	C39—C35—C36	115.2 (3)
C5—N3—Co1	115.2 (3)	C39—C35—C18	121.5 (3)
O3—N3—Co1	123.1 (2)	C36—C35—C18	123.3 (3)
N3—O3—H3	109.5	C37—C36—C35	120.7 (3)
C6—N4—O4	123.3 (3)	C37—C36—H36	119.6
C6—N4—Co1	115.2 (3)	C35—C36—H36	119.6
O4—N4—Co1	121.5 (2)	N5—C37—C36	122.7 (3)
N3—C5—C6	113.4 (3)	N5—C37—H37	118.6
N3—C5—C7	121.9 (6)	C36—C37—H37	118.6
C6—C5—C7	124.7 (5)	N5—C38—C39	122.4 (3)
N4—C6—C5	113.8 (3)	N5—C38—H38	118.8
N4—C6—C8	122.1 (6)	C39—C38—H38	118.8
C5—C6—C8	124.0 (5)	C38—C39—C35	121.5 (3)
C5—C7—H7A	109.5	C38—C39—H39	119.3
C5—C7—H7B	109.5	C35—C39—H39	119.3
H7A—C7—H7B	109.5	C41—C40—C45	116.9 (4)
C5—C7—H7C	109.5	C41—C40—C23	123.5 (4)
H7A—C7—H7C	109.5	C45—C40—C23	119.4 (4)
H7B—C7—H7C	109.5	C40—C41—C42	120.1 (6)
C6—C8—H8A	109.5	C40—C41—H41	120.0
C6—C8—H8B	109.5	C42—C41—H41	120.0
H8A—C8—H8B	109.5	C43—C42—C41	121.6 (7)
C6—C8—H8C	109.5	C43—C42—H42	119.2
H8A—C8—H8C	109.5	C41—C42—H42	119.2
H8B—C8—H8C	109.5	C44—C43—C42	120.2 (6)
C37—N5—C38	117.5 (2)	C44—C43—H43	119.9
C37—N5—Co1	122.63 (19)	C42—C43—H43	119.9
C38—N5—Co1	119.84 (19)	C43—C44—C45	120.2 (7)
C9—N6—C12	108.5 (2)	C43—C44—H44	119.9
C9—N6—H6	125.7	C45—C44—H44	119.9
C12—N6—H6	125.7	C40—C45—C44	121.0 (6)
C24—N7—C27	105.8 (2)	C40—C45—H45	119.5
C19—N8—C22	109.2 (2)	C44—C45—H45	119.5
C19—N8—H8	125.4	C47—C46—C51	117.7 (3)
C22—N8—H8	125.4	C47—C46—C28	122.1 (3)
C17—N9—C14	106.6 (2)	C51—C46—C28	120.1 (3)
N6—C9—C28	126.1 (3)	C48—C47—C46	121.5 (4)

N6—C9—C10	107.7 (3)	C48—C47—H47	119.2
C28—C9—C10	126.2 (3)	C46—C47—H47	119.2
C11—C10—C9	107.9 (3)	C49—C48—C47	120.7 (5)
C11—C10—H10	126.1	C49—C48—H48	119.7
C9—C10—H10	126.1	C47—C48—H48	119.7
C10—C11—C12	108.0 (3)	C48—C49—C50	120.9 (4)
C10—C11—H11	126.0	C48—C49—H49	119.5
C12—C11—H11	126.0	C50—C49—H49	119.5
N6—C12—C13	126.5 (3)	C49—C50—C51	119.0 (4)
N6—C12—C11	107.9 (3)	C49—C50—H50	120.5
C13—C12—C11	125.6 (3)	C51—C50—H50	120.5
C14—C13—C12	125.9 (3)	C46—C51—C50	120.0 (4)
C14—C13—C29	118.0 (3)	C46—C51—H51	120.0
C12—C13—C29	116.1 (3)	C50—C51—H51	120.0
N9—C14—C13	126.1 (3)	C11B—C1A—C12A	150.6 (6)
N9—C14—C15	109.5 (3)	C11B—C1A—C13B	104.8 (16)
C13—C14—C15	124.5 (3)	C12A—C1A—C13B	62.6 (12)
C16—C15—C14	107.8 (3)	C11B—C1A—C12B	111.7 (11)
C16—C15—H15	126.1	C12A—C1A—C12B	48.6 (8)
C14—C15—H15	126.1	C13B—C1A—C12B	95.2 (12)
C15—C16—C17	106.8 (3)	C11B—C1A—C13A	60.0 (6)
C15—C16—H16	126.6	C12A—C1A—C13A	113.2 (5)
C17—C16—H16	126.6	C13B—C1A—C13A	50.6 (11)
N9—C17—C18	125.3 (3)	C12B—C1A—C13A	131.5 (11)
N9—C17—C16	109.3 (3)	C11B—C1A—C11A	52.1 (6)
C18—C17—C16	125.3 (3)	C12A—C1A—C11A	111.6 (4)
C17—C18—C19	125.2 (3)	C13B—C1A—C11A	125.9 (15)
C17—C18—C35	117.3 (3)	C12B—C1A—C11A	63.2 (9)
C19—C18—C35	117.1 (3)	C13A—C1A—C11A	106.1 (4)
N8—C19—C18	125.9 (3)	C11B—C1A—H1A	100.3
N8—C19—C20	107.8 (3)	C12A—C1A—H1A	108.6
C18—C19—C20	126.3 (3)	C13B—C1A—H1A	124.6
C21—C20—C19	107.6 (3)	C12B—C1A—H1A	119.8
C21—C20—H20	126.2	C13A—C1A—H1A	108.6
C19—C20—H20	126.2	C11A—C1A—H1A	108.6
C20—C21—C22	108.3 (3)	C1A—C12B—C13B	42.1 (6)
C20—C21—H21	125.8	C1A—C13B—C12B	42.7 (7)

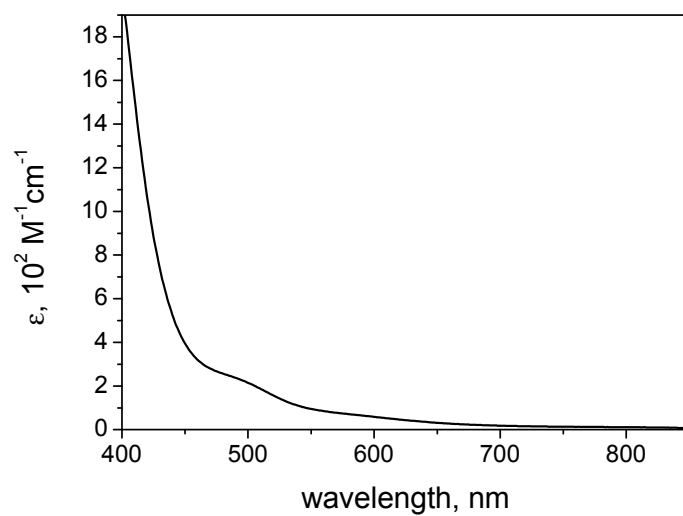


Figure S4. Absorption spectrum of model compound $\text{Co}(\text{dmgH})_2\text{Cl}(\text{EtPy})$ in THF.

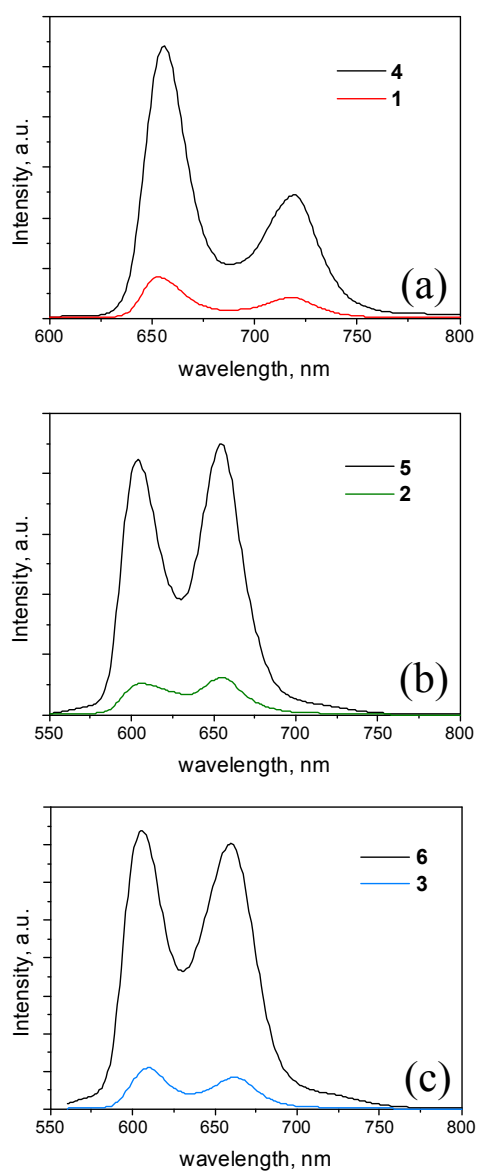


Figure S5. Comparison of emission spectra in THF (ca. 1×10^{-5} M) of optically matched solutions at the excitation wavelength of (a) **1** and **4** (excitation at 530 nm), (b) **2** and **5** (excitation at 530 nm), and (c) **3** and **6** (excitation at 550 nm).

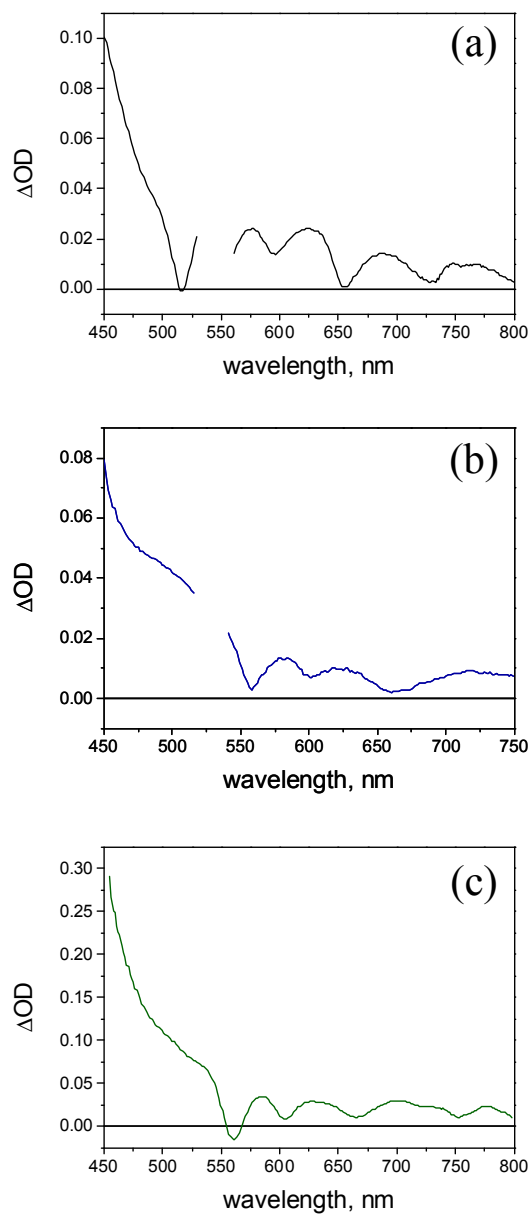


Figure S6. Excited singlet state difference absorption spectra obtained by Ultrafast Spectroscopy in THF on the molecular models (a) **4** (excitation at 550 nm), (b) **5** (excitation at 530 nm), and (c) **6** (excitation at 550 nm).

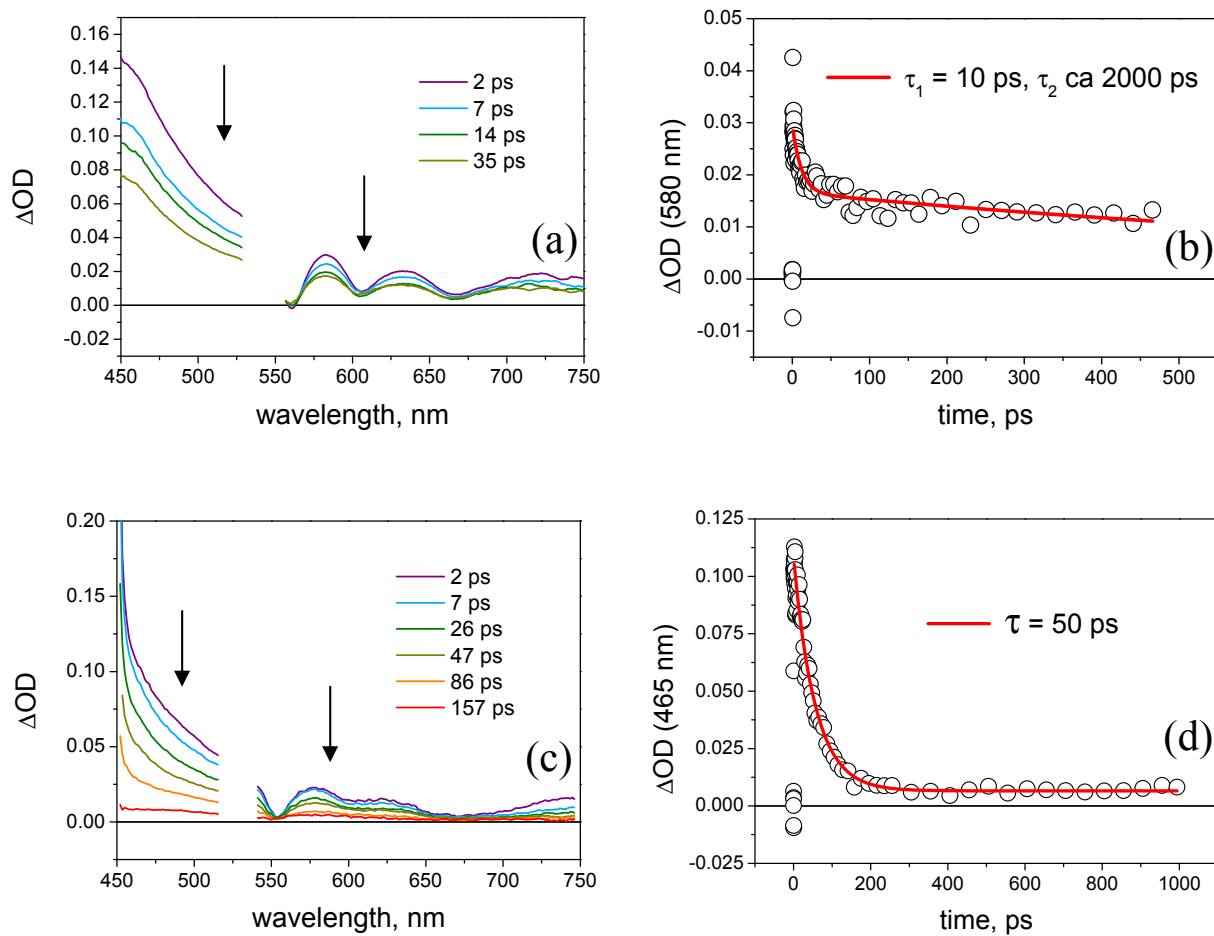


Figure S7. (a) Difference absorption spectra obtained by ultrafast spectroscopy in DMF for **2** (excitation at 550 nm), (b) kinetic analysis at 580 nm and relative fitting; (c) difference absorption spectra obtained by ultrafast spectroscopy in toluene for **2** (excitation at 530 nm), (d) kinetic analysis at 465 nm and relative fitting.

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