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Supporting Information

(Pentamethylcyclopentadienyl)ruthenium *p*-Complexes of Metalloporphyrins: Platforms with Novel Photo-and Electrochemical Properties

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Supporting Information

General experimental procedures. Prior to use, all glassware was soaked in KOH-saturated isopropyl alcohol for ca. 12 h and then rinsed with water and acetone before being thoroughly dried. Dichloromethane was freshly distilled from CaH_2. *n*-pentane was stirred over concentrated H_2SO_4 for more than 24h, neutralized with K_2CO_3, and distilled from CaH_2. Zinc(II), Copper (II) and Ni(II) metallo-octaethylporphyrins were purchased commercially (Aldrich) and used as received, and $[Ru(Cp^*)(CH_3CN)_3][PF_6]$ was prepared following reported procedures.[1] Solutions were stirred magnetically.

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Mercury 400 MHz. High-resolution mass spectra were obtained at the University of Texas at Austin, Department of Chemistry and Biochemistry, Mass Spectrometry Facility. Elemental analyses were performed by Midwest Microlabs Inc., Indianapolis, IN.

Synthetic details:

Compound 1: $[Ru(Cp^*)(CH_3CN)_3][PF_6]$ (40 mg, 0.08 mmol) was added to a solution of Ni(II)-octaethylporphyrin (35 mg, 0.06 mmol) in dry CH_2Cl_2 (30 mL) under argon atmosphere. The reaction mixture is refluxed during 6h. The solvent was then evaporated to a volume of 5 mL, and the resulting solution was purified by means of thin layer chromatography (alumina, CH_2Cl_2). The olive green fraction was collected and the resulting product was recrystallized from CH_2Cl_2/*n*-pentane to yield 37 mg of complex **1** (72 %). ^{1}H NMR (400 MHz, 296 K, $CDCl_3$): 8.62 (s, 2H, *meso*-H), 8.40 (s, 2H, *meso*-H), 3.45-3.37 (m, 12H, CH_2), 3.11 (q (J = 7.5 Hz), 4H, CH_2), 1.62-1.56 (m, 18H, CH_3), 1.49 (t (J = 7.5 Hz), 6H, CH_3), 0.98 (s, 15H, C_5Me_5). ^{13}C NMR (100.6 MHz, 296 K, $CDCl_3$): 153.9, 150.9, 148.1, 146.5, 142.8, 142.3, 109.4, 103.0, 99.2, 95.0, 86.8, 29.9, 19.3, 19.1, 18.2, 18.0, 17.5, 17.3, 17.1, 9.7. HR-ESI (m/z): 827.3131 (calc. For $C_{46}H_{59}N_4NiRu^{1+}$: 827.3138). Anal. Calcd. for **1**$\cdot(CH_2Cl_2)_2$ $C_{48}H_{63}Cl_4F_6N_4NiP_6Ru$: C, 50.46; H, 5.56; N, 4.90. Found: C, 50.29; H, 5.67; N, 4.78.

Compound 2: A solution of Cu(II)-octaethylporphyrin (36 mg, 0.06 mmol) and $[Ru(Cp^*)(CH_3CN)_3][PF_6]$ (40 mg, 0.08mmol) in dry CH_2Cl_2 (30 mL) was heated to reflux during 6h in argon atmosphere. Upon concentrating to a volume of 5 ml, the compound was purified by thin layer chromatography (alumina, CH_2Cl_2). The olive green fraction was collected and the resulting product was crystallized by slow diffusion of *n*-pentane into a saturated solution of **2** in CH_2Cl_2 at -40 ºC. Yield: 34 mg (65 %). HR-ESI (m/z): 832.3073 (calc. For $C_{46}H_{59}N_4CuRu^{1+}$: 832.3076) Anal. Calcd. for **2**$\cdot(CH_2Cl_2)_2$ $C_{48}H_{63}Cl_4F_6N_4CuP_6Ru$: C, 50.24; H, 5.53; N, 4.88. Found: C, 50.11; H, 5.49; N, 4.63.

Compound 3: $[Ru(Cp^*)(CH_3CN)_3][PF_6]$ (40 mg, 0.08mmol) was added to a solution of Zn(II)-Octaethylporphyrin (36 mg, 0.06 mmol) in dry CH_2Cl_2 (30 mL) under argon atmosphere. The reaction mixture is refluxed during 6h, allowed to cool and then concentrated to a volume of 5 mL. Purification by means of thin layer chromatography (alumina, 1% MeOH/CH_2Cl_2) afford the compound **3** as a dark green solid. (24 mg, 46 %). Crystals of **3** were obtained by slow diffusion of *n*-pentane into a saturated solution of the compound in CH_2Cl_2 at -40 ºC. ^{1}H NMR (400 MHz, 296 K, CD_2Cl_2): 8.54 (s, 2H, *meso*-H), 8.39 (s, 2H, *meso*-H), 3.45-3.38 (m, 12H, CH_2), 3.13 (q (J = 7.5 Hz), 4H, CH_2), 1.61-1.49 (m, 24H, CH_3), 0.48 (s, 15H, C_5Me_5). ^{13}C NMR (100.6 MHz, 296 K, CD_2Cl_2): 161.7, 159.5, 148.3, 147.5, 146.0, 142.9, 109.8, 103.9, 85.0, 73.8, 66.0, 29.9, 19.0, 18.3, 18.1, 17.6, 17.2, 17.1, 17.0, 9.0. HR-ESI (m/z): 833.3069 (calc. For $C_{46}H_{59}N_4ZnRu^{1+}$: 833.3064). Anal. Calcd. for **3**$\cdot(CH_2Cl_2)_2$ $C_{48}H_{63}Cl_4F_6N_4ZnP_6Ru$: C, 50.16; H, 5.53; N, 4.87. Found: C, 50.07; H, 5.41; N, 4.59.

X-ray experimental

The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). Data collections were conducted at 153 K using an Oxford Cryostream low temperature device.
Data reductions were performed using DENZO-SMN.[2] The structures were solved by direct methods using SIR97[3] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[4]

The following definitions apply to all the refinements:

$R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$ for reflections with $F_0 > 4(\Sigma\ (F_0))$,

$R_W = \{\Sigma w(|F_0|^2 - |F_c|^2)^2/\Sigma w|F_0|^4\}^{1/2}$, where w is the weight given each reflection,

Goodness of fit, $S = [\Sigma w(|F_0|^2 - |F_c|^2)^2/(n - p)]^{1/2}$,

where n is the number of reflections and p is the number of refined parameters.

Unless otherwise specified, hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 × Ueq of the attached atom (1.5 × Ueq for methyl hydrogen atoms). Neutral atom scattering factors and values used to calculate the linear absorption coefficients are from the International Tables for X-ray Crystallography.[5]

X-ray experimental for Compound 2:

Crystals grew as dark, almost black needles by slow diffusion of *n*-pentane into a saturated solution of **2** in CH_2Cl_2 at -40 ºC. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 598 frames of data were collected using ω-scans with a scan range of 0.6° and a counting time of 72 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[2] The structure was solved by direct methods using SIR97[3] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[4] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.02{*}P)^2]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_W(F^2)$ refined to 0.153, with R(F) equal to 0.0907 and a goodness of fit, S, = 1.25. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit, S, are given below.[5] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[6] All figures were generated using SHELXTL/PC.[7]

X-ray experimental for compound 3:

Crystals grew as very small, black prisms by slow diffusion of pentane into a dichloromethane solution of **3**. The data crystal was a prism that had approximate dimensions; 0.06 x 0.06 x 0.05 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 298 frames of data were collected using ω-scans with a scan range of 1.2° and a counting time of 222 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using DENZO-SMN.[2] The structure was solved by direct methods using SIR97[3] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[4] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

Two molecules of dichloromethane were badly disordered. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE in PLATON98.[8] PLATON98 was used as incorporated in WinGX.[9]

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.02*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_W(F^2)$ refined to 0.165, with R(F) equal to 0.0802 and a goodness of fit, S, = 1.13. Definitions used for calculating R(F), $R_W(F^2)$ and the goodness of fit, S, are given below.[5] The data were checked for secondary extinction but no correction was needed. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[6] All figures were generated using SHELXTL/PC.[7]

Table S1 Crystal data and structure refinement parameters for complexes **2** and **3**.

	2	**3**
empirical formula	$C_{46}H_{59}CuF_6N_4PRu\cdot(CH_2Cl_2)_2$	$C_{46}H_{59}F_6N_4PRuZn\cdot(CH_2Cl_2)_2$
formula weight	1147.40	1149.23
crystal system	triclinic	triclinic
space group	P-1	P-1
a, Å	10.191(2)	10.4590(5)
b, Å	15.570(2)	15.7622(7)
c, Å	17.858(3)	18.152(1)
a, º	110.550(6)	112.100(2)
ß, º	105.170(7)	93.280(2)
?, º	90.970(7)	105.280(2)
V, Å^3	2542.2(7)	2633.3(17)
Z	2	2
D (Calc'd), mg/m^3	1.499	1.449
abs. coeff., mm^{-1}	1.016	1.033
F(000)	1178	1180
q for data collection, º	2.11 - 25.05	2.05 - 24.87
limiting indices	- 12 = h = 12	-12 = h = 11
	- 17 = k =18	- 18 = k =18
	- 21= l = 18	- 21 = l = 19
reflections collected	13316	15375
independent reflections	8315	8838
completeness to q_{max}	92.3 %	96.5 %
absorption correction	none	none
data/restraints/parameters	8315/ 88 / 610	8838 / 60 / 545
goodness-of-fit on F^2	1.217	1.106
R, R_w	0.0907, 0.1175	0.0802, 0.1470

References

1) B. Steinmetz, W. A. Schenk. *Organometallics* **1999**, *18*, 943-946.

2) DENZO-SMN. (1997). Z. Otwinowski, W. Minor. Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326. C. W. Carter Jr., R. M. Sweets. Editors, Academic Press.

3) SIR97. (1999). A program for crystal structure solution. A. Altomare, M. C. Burla, M. Camalli, , G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna. *J. Appl. Cryst.* 32, 115-119.

4) G. M. Sheldrick, (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

5) $R_W(F^2) = \{\Sigma w(|F_O|^2 - |F_C|^2)^2/\Sigma w(|F_O|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_O| - |F_C|)/\Sigma|F_O|\}$ for reflections with $F_O > 4(\sigma(F_O))$.
$S = [\Sigma w(|F_O|^2 - |F_C|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

6) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

7) G. M. Sheldrick, (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

8) A. L. Spek. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.

9) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. L. J. J. Farrugia. J. *Appl. Cryst.* 32. 837-838.

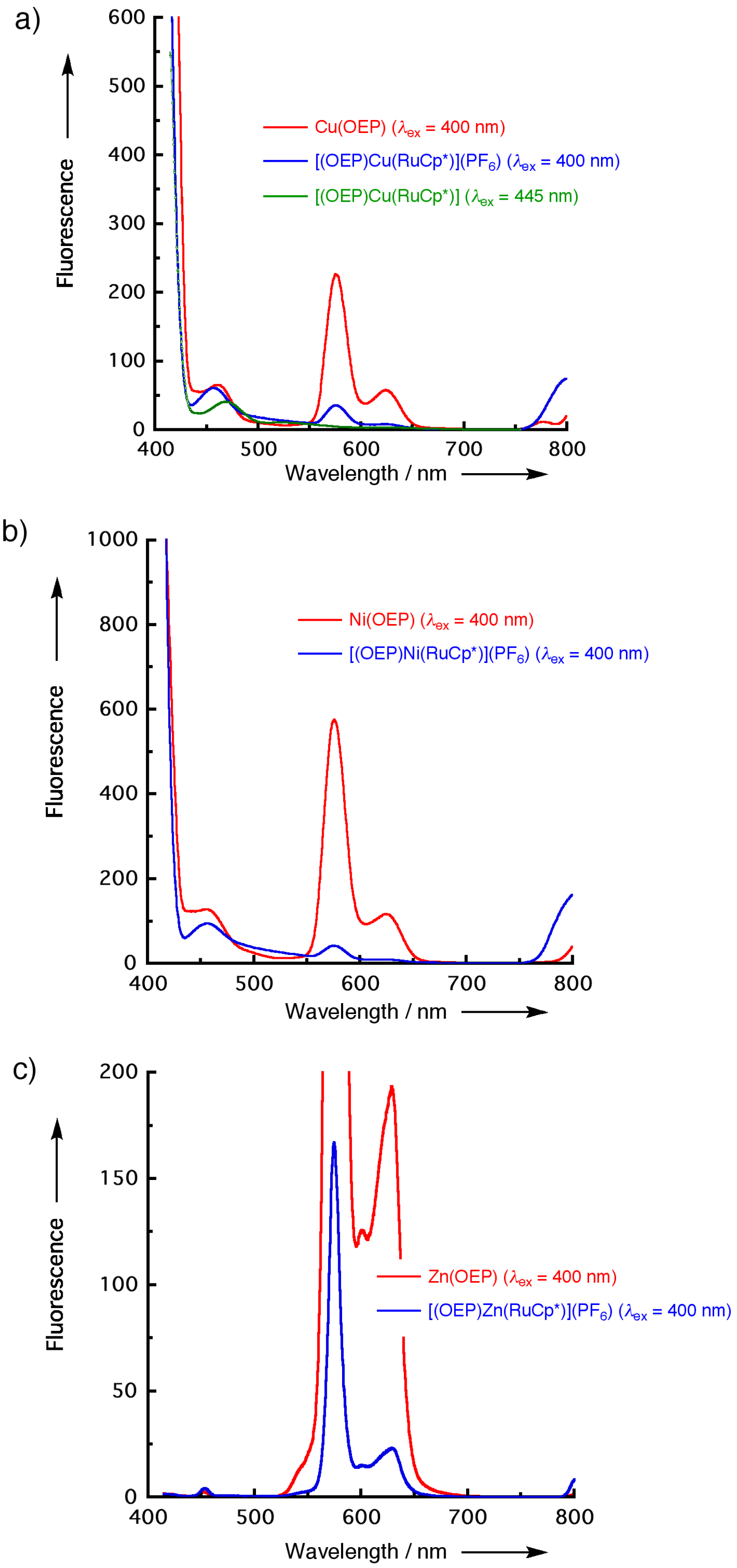

Figure S1. Fluorescence spectra of **1-3** in comparison with those of Ni(OEP), Cu(OEP) and Zn(OEP), respectively.

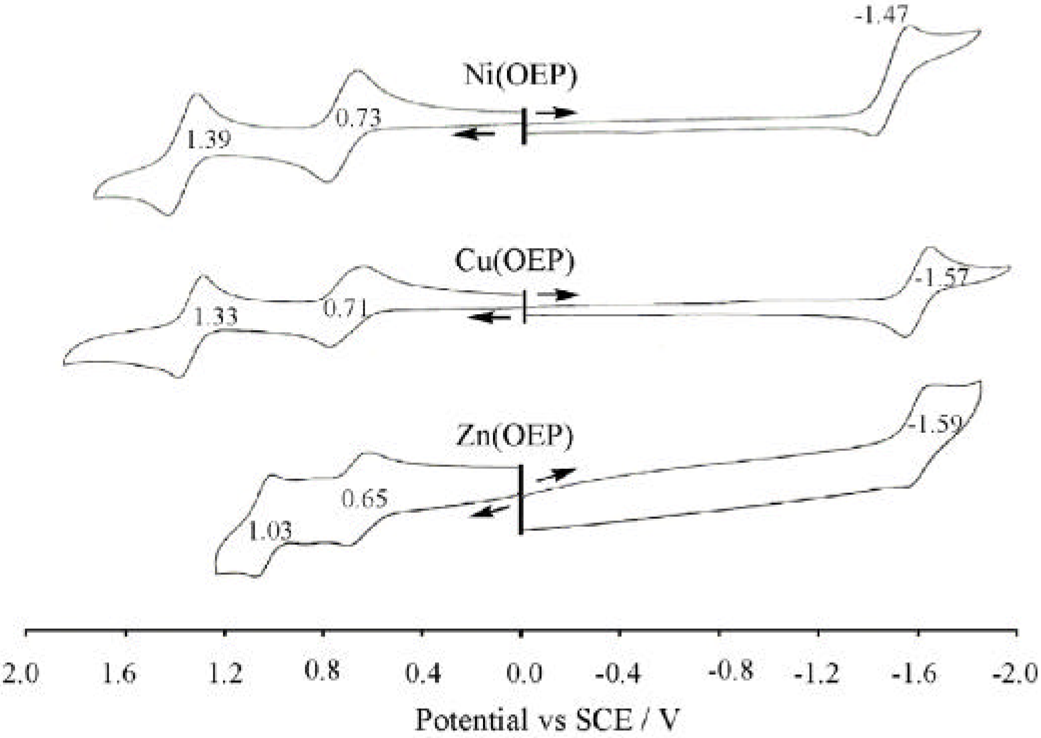

***Figure S2*.** Cyclic voltammograms of Ni(OEP), Cu(OEP) and Zn(OEP) in CH_2Cl_2 containing 0.10 M $TBAPF_6$.

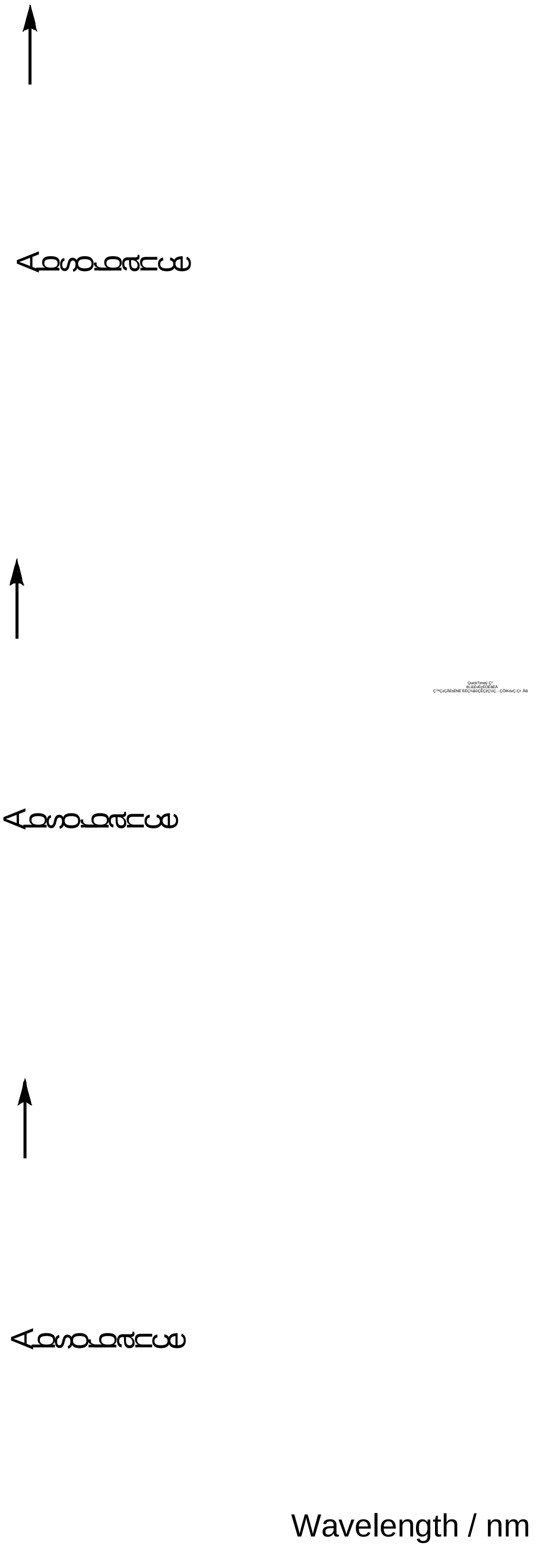

***Figure S3*.** Spectroelectrochemical data for the oxidation of **1** in CH_2Cl_2 at room temperature.

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***Figure S4*.** Spectroelectrochemical data for the reduction of **1** in CH_2Cl_2 at room temperature.

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***Figure S5*.** Spectroelectrochemical data for the reduction of **2** in THF at room temperature.

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***Figure S6*.** Spectroelectrochemical data for the oxidation of **2** in CH_2Cl_2 at room temperature.

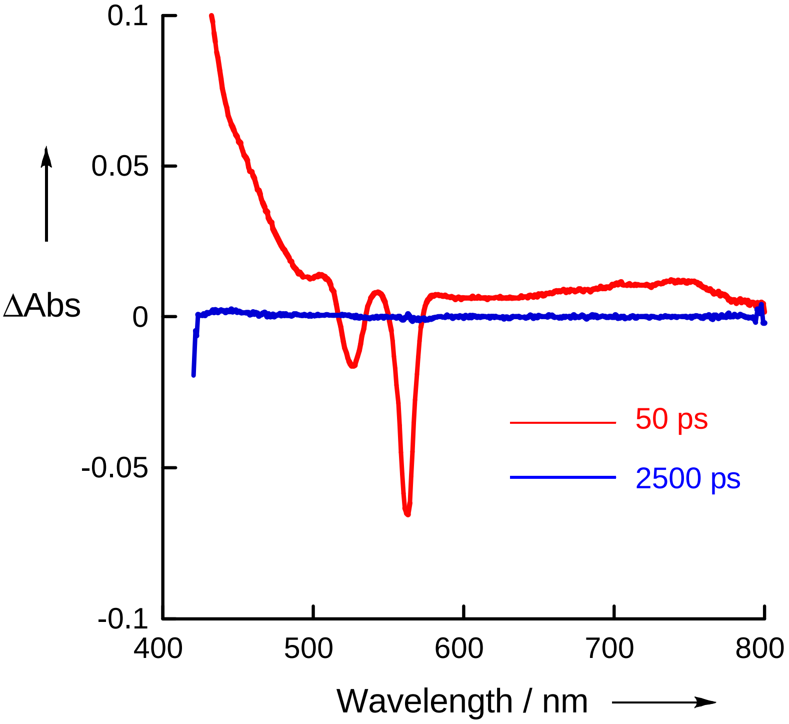

Figure S7. Transient absorption spectra of Cu(OEP) in THF after femtosecond laser pulse irradiation by the 410 nm laser at the indicated time intervals at 298 K.

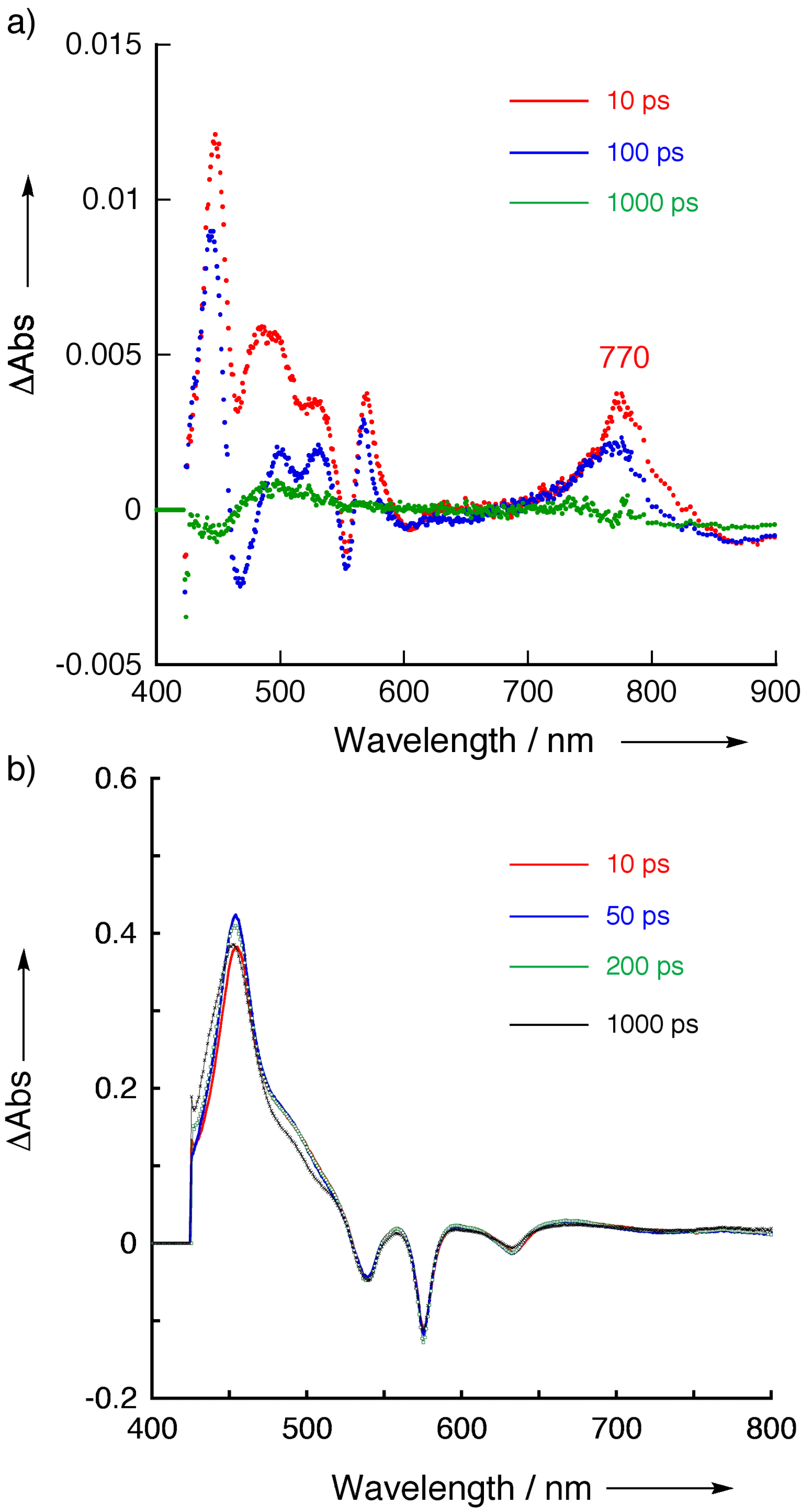

Figure S8. Transient absorption spectra of a) **1** and b) **3** in THF after femtosecond laser pulse irradiation by the 410 nm laser at the indicated time intervals at 298 K.

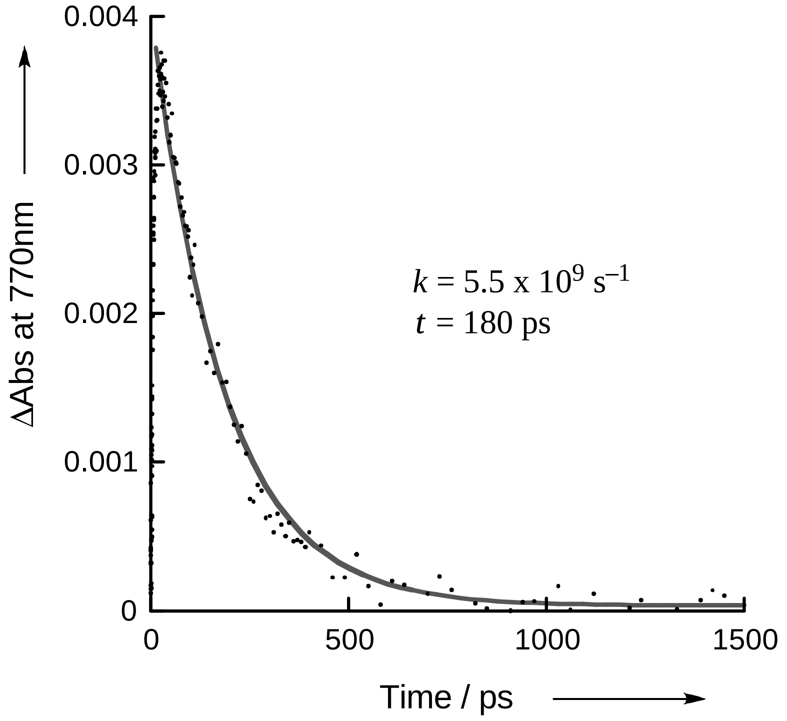

Figure S9. Decay time profile of the absorbance feature at 770 nm observed following femtosecond laser photoexcitation of **1** in THF.

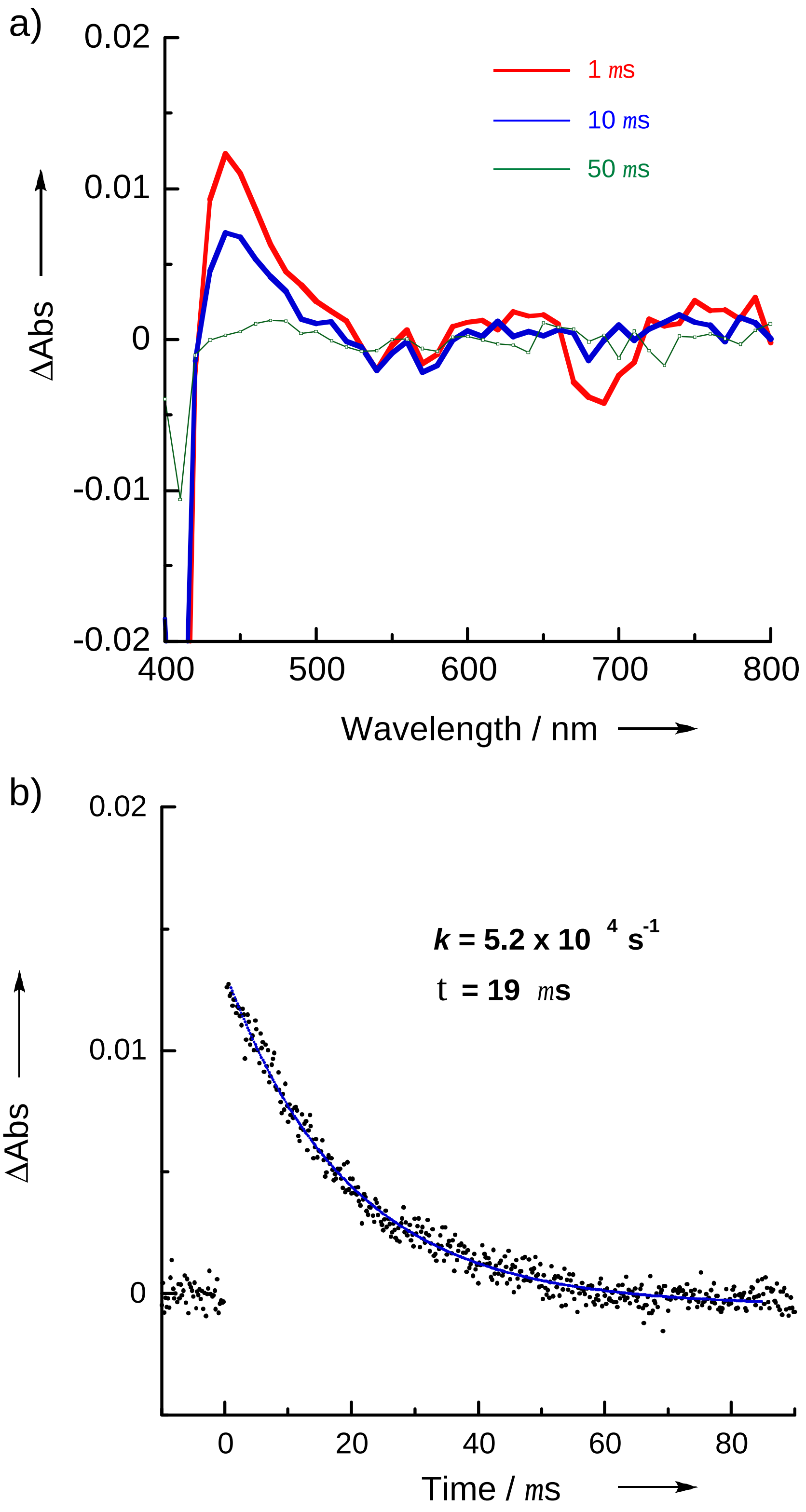

Figure S10. a) Transient absorption spectra of **3** in THF after nanosecond laser pulse irradiation by the 410 nm laser at the indicated time intervals at 298 K. b) Decay time profile at 450 nm.