Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary data

Synthesis and photochemical properties of *a*-diketoporphyrins as precursors for π-expanded porphyrins

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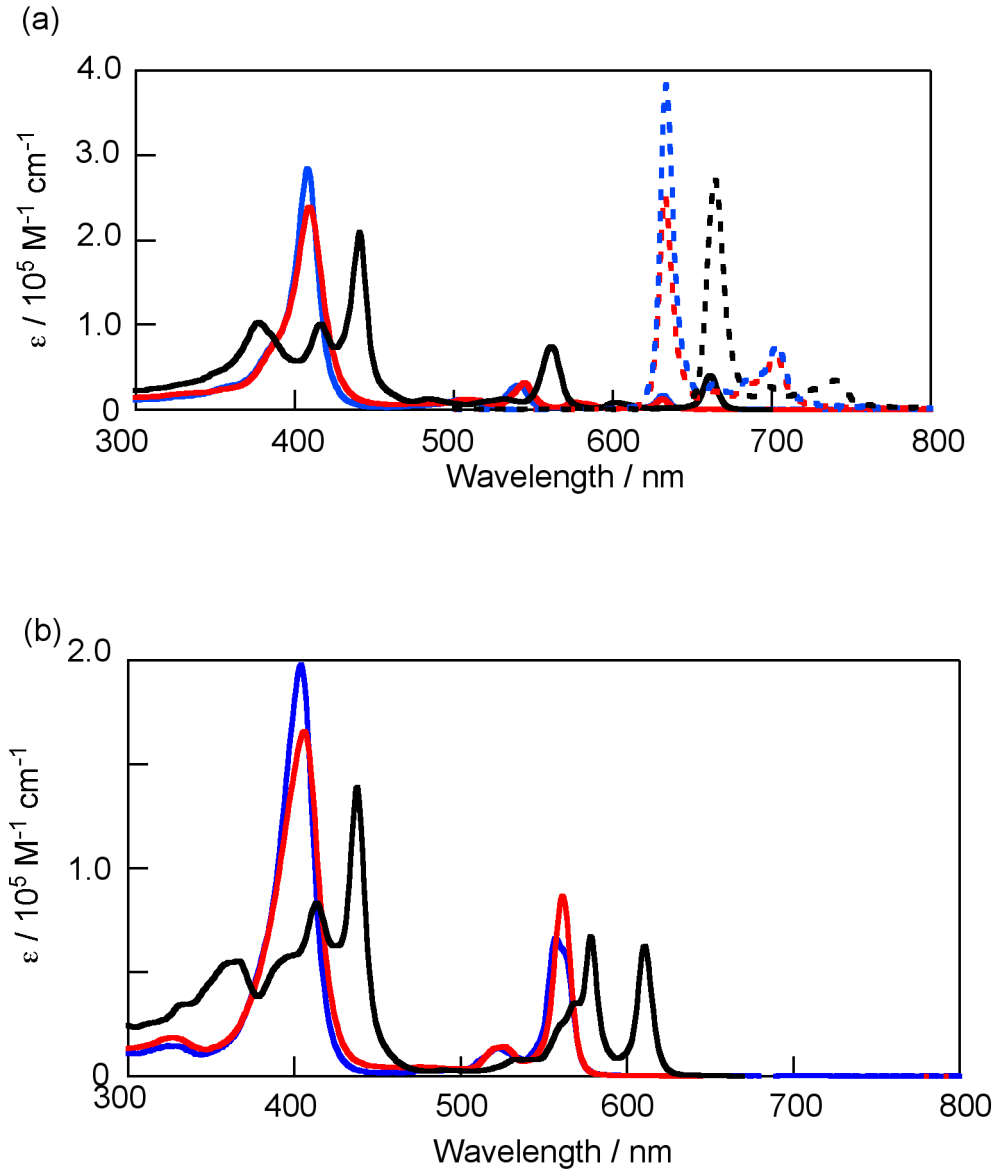


Fig S1 (a) UV-vis (solid lines) and fluorescence (broken lines) spectra in toluene of **H_2P-DOHa** (blue), **H_2P-DK** (red), and **H_2P-mA** (black), and b) UV-vis spectra in toluene of **PdP-DOHa** (blue), **PdP-DK** (red), and **PdP-mA** (black). Fluorescence spectra were measured at 7.0×10^{-7} M.

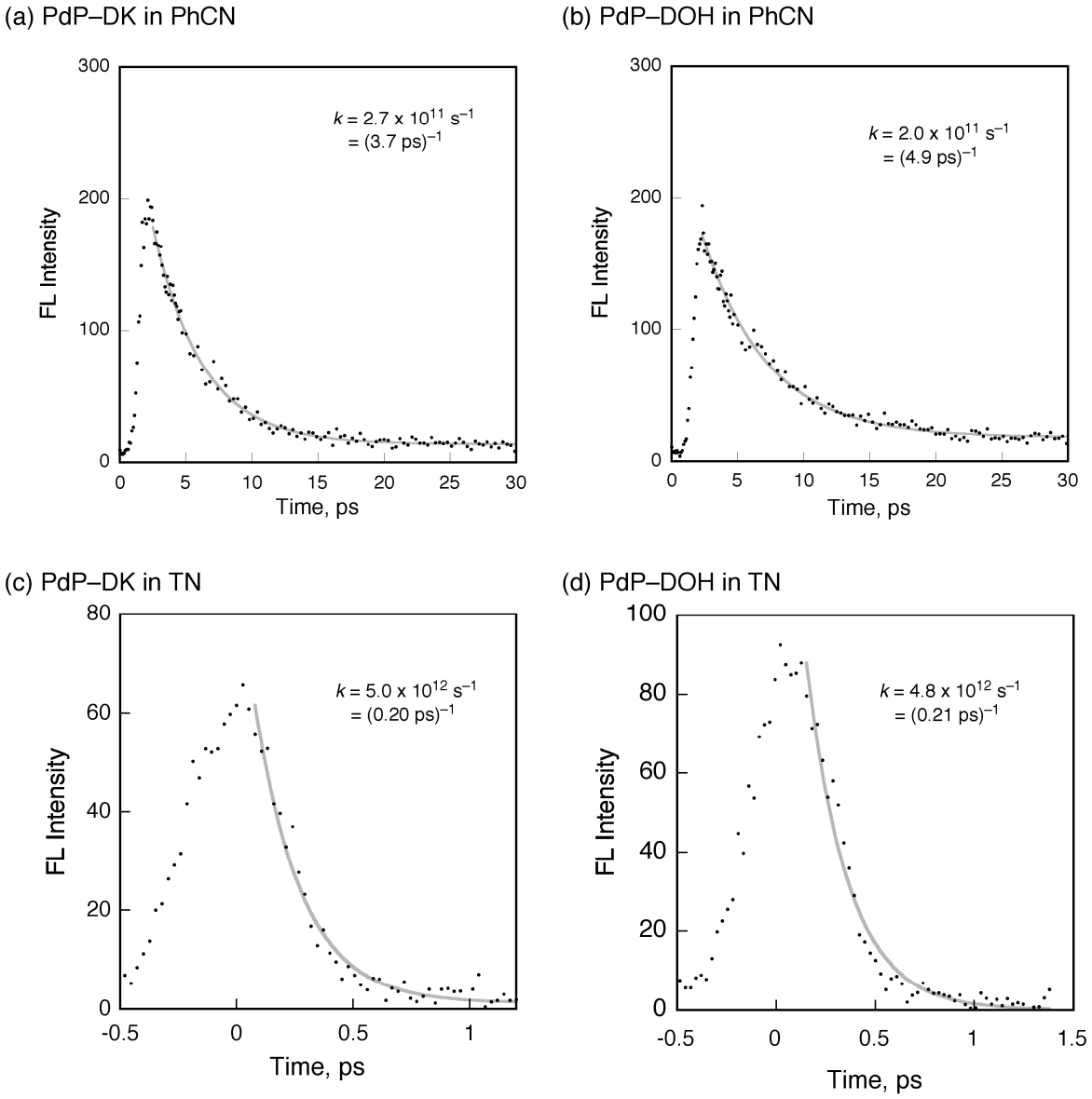
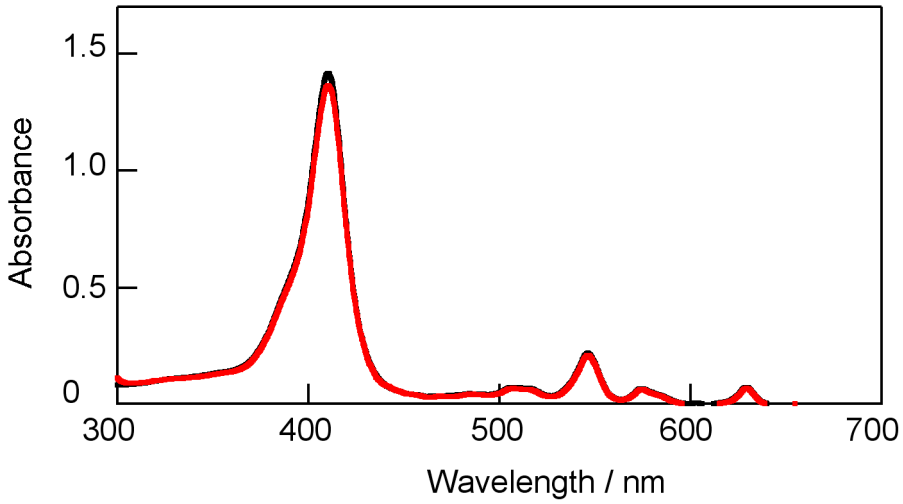


Fig S2 Fluorescence decay curves of (a) **PdP-DK** in PhCN, (b) **PdP-DOHa** in PhCN, (c) **PdP-DK** in toluene, and (d) **PdP-DOHa** in toluene; λ_{EX} = 410 nm; λ_{obs} = 630 nm.

(a)



(b)

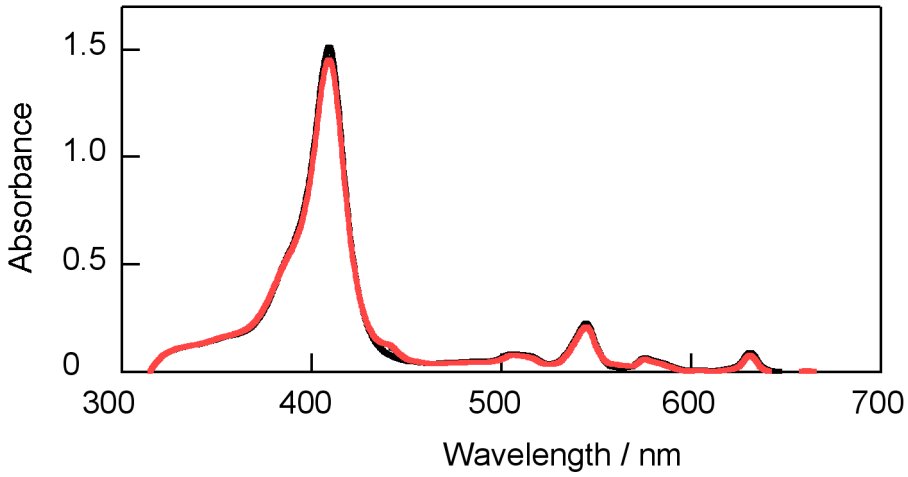


Fig S3 Changes of absorption spectra during photocleavage reaction of **H_2P-DK**. (a) λ_{EX} = 544 nm; 1.04 $\times 10^{-5}$ M in PhCN; 0 (black solid line), 10, 20, 30, 40, and 50 (black broken lines), and 60 min (red solid line); (b) λ_{EX} = 544 nm; 9.77 $\times 10^{-6}$ M in toluene; 0 (black solid line), 10, 20, 30, 40, and 50 (black broken lines), and 60 min (red solid line).

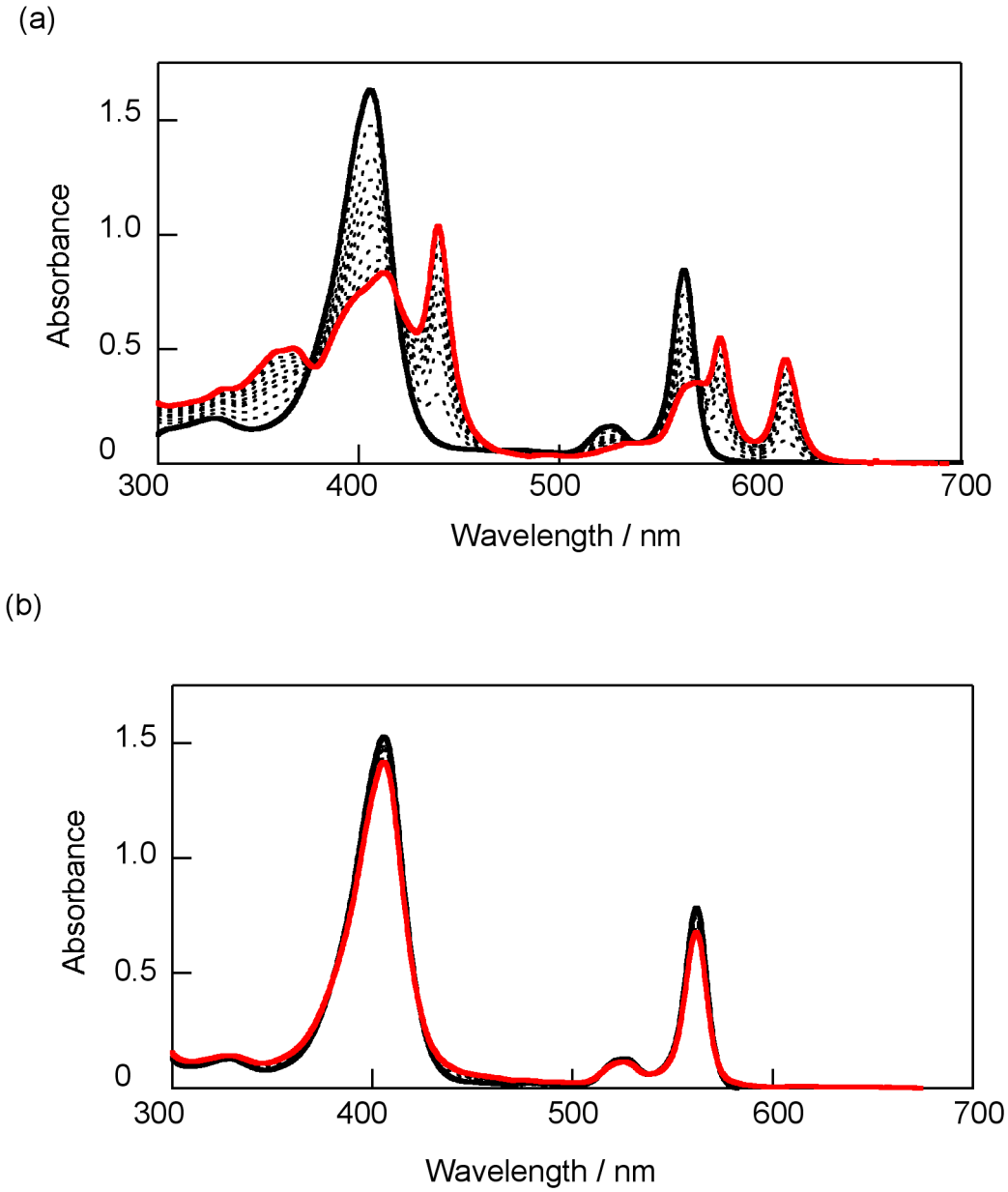


Fig S4 Changes of absorption spectra during photocleavage reaction of **PdP-DK**. (a) λ_{EX} = 406 nm; 1.04×10^{-5} M in PhCN; 0 (black solid line), 10, 20, 30, 40, 50, 60, 80, 100, 120 (black broken lines), and 140 min (red solid line); (b) λ_{EX} = 561 nm; 9.77×10^{-6} M in PhCN 0 (black solid line), 20, 40, 60, 80, 100, 120, (black broken lines), and 140 min (red solid line).

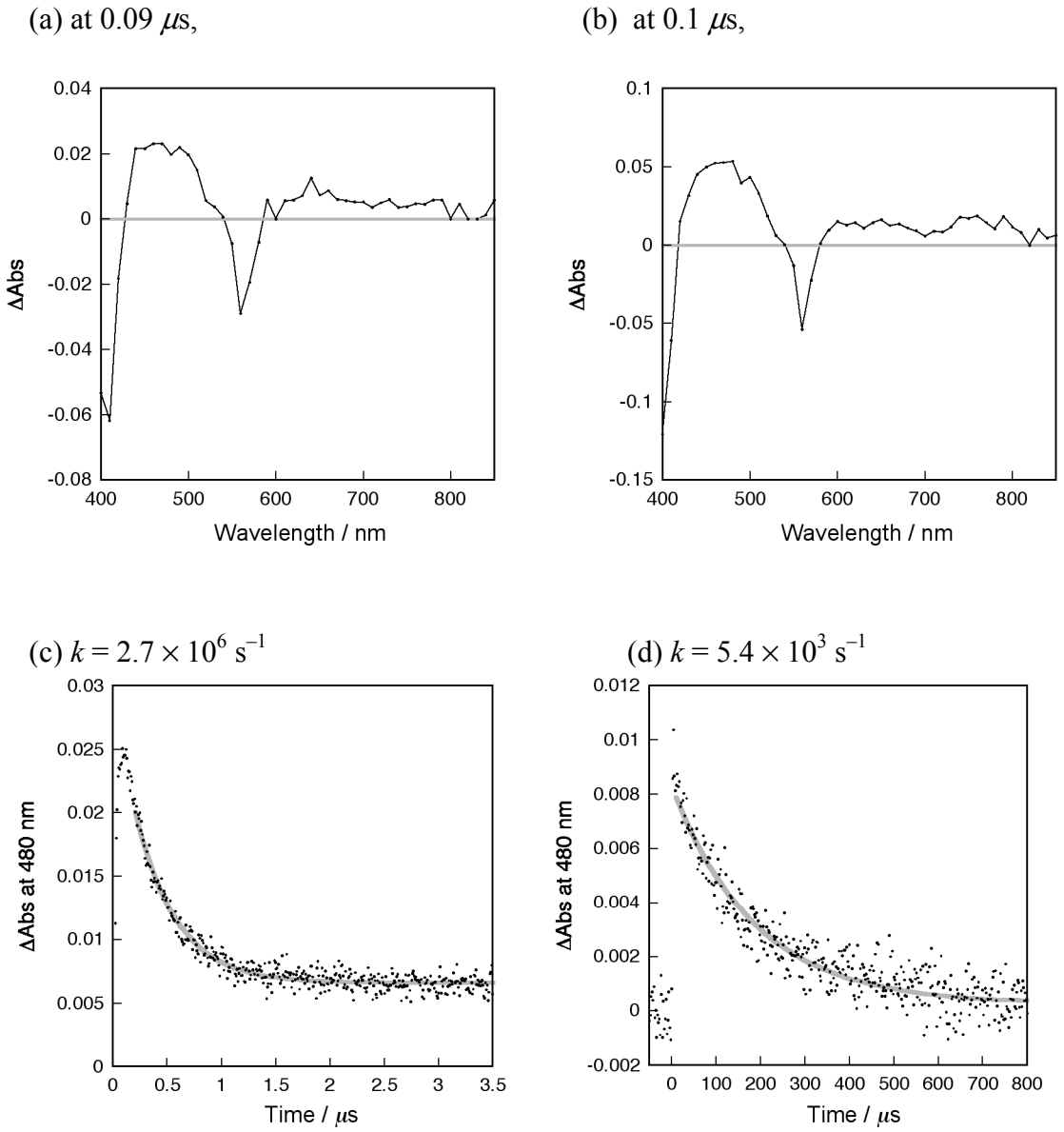


Fig S5 Nanosecond transient absorption spectra of **PdP-DK** in (a) PhCN at 0.09 μs; (b) toluene at 0.1 μs; and its decay curves in (c) PhCN; (d) toluene; excited by 426 nm laser flash.

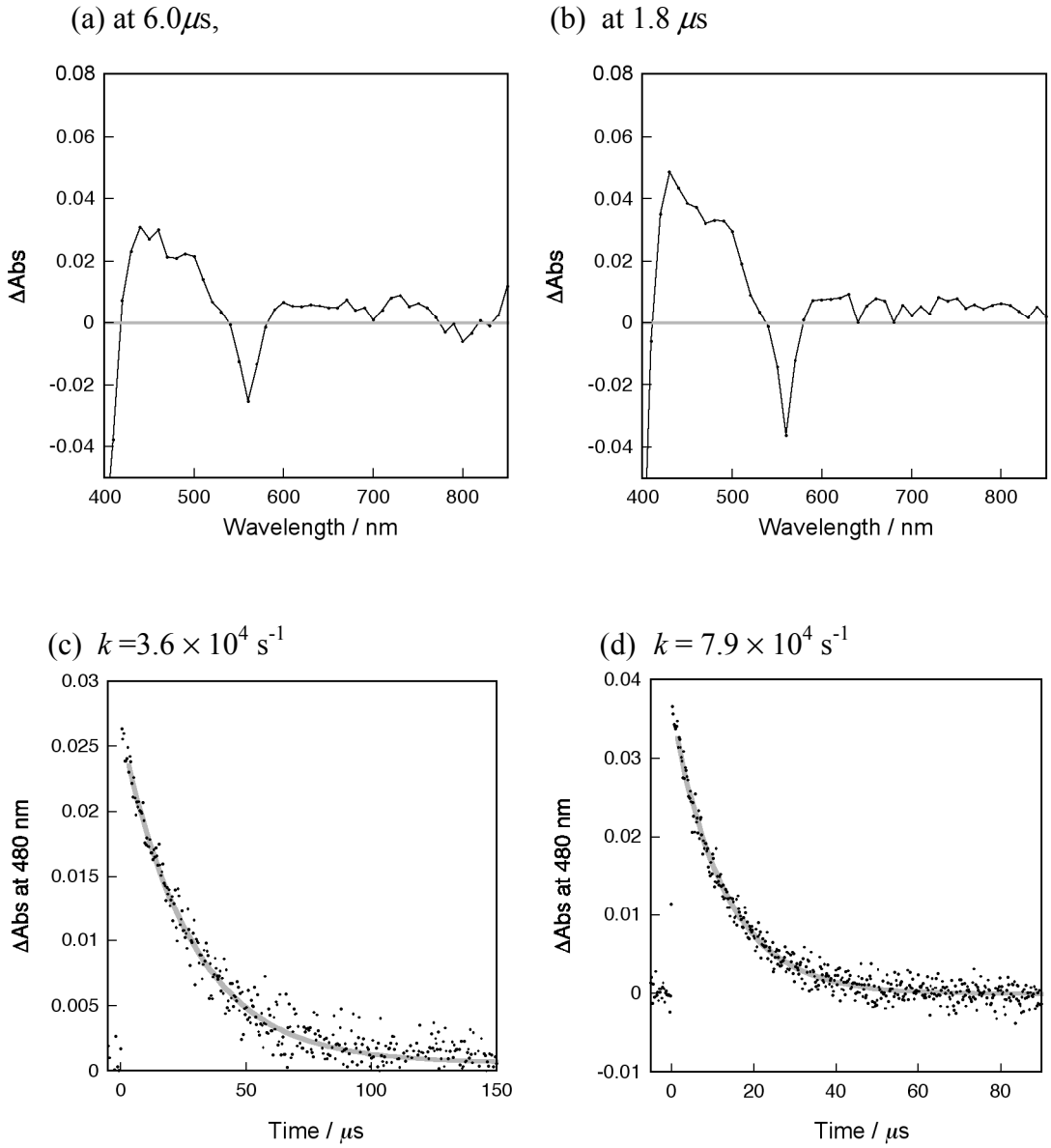


Fig S6 Nanosecond transient absorption spectra of **PdP-DOHa** in (a) PhCN at 6.0 μs; (b) toluene at 1.8 μs; and its decay curves in (c) PhCN; (d) toluene; excited by 426 nm laser.

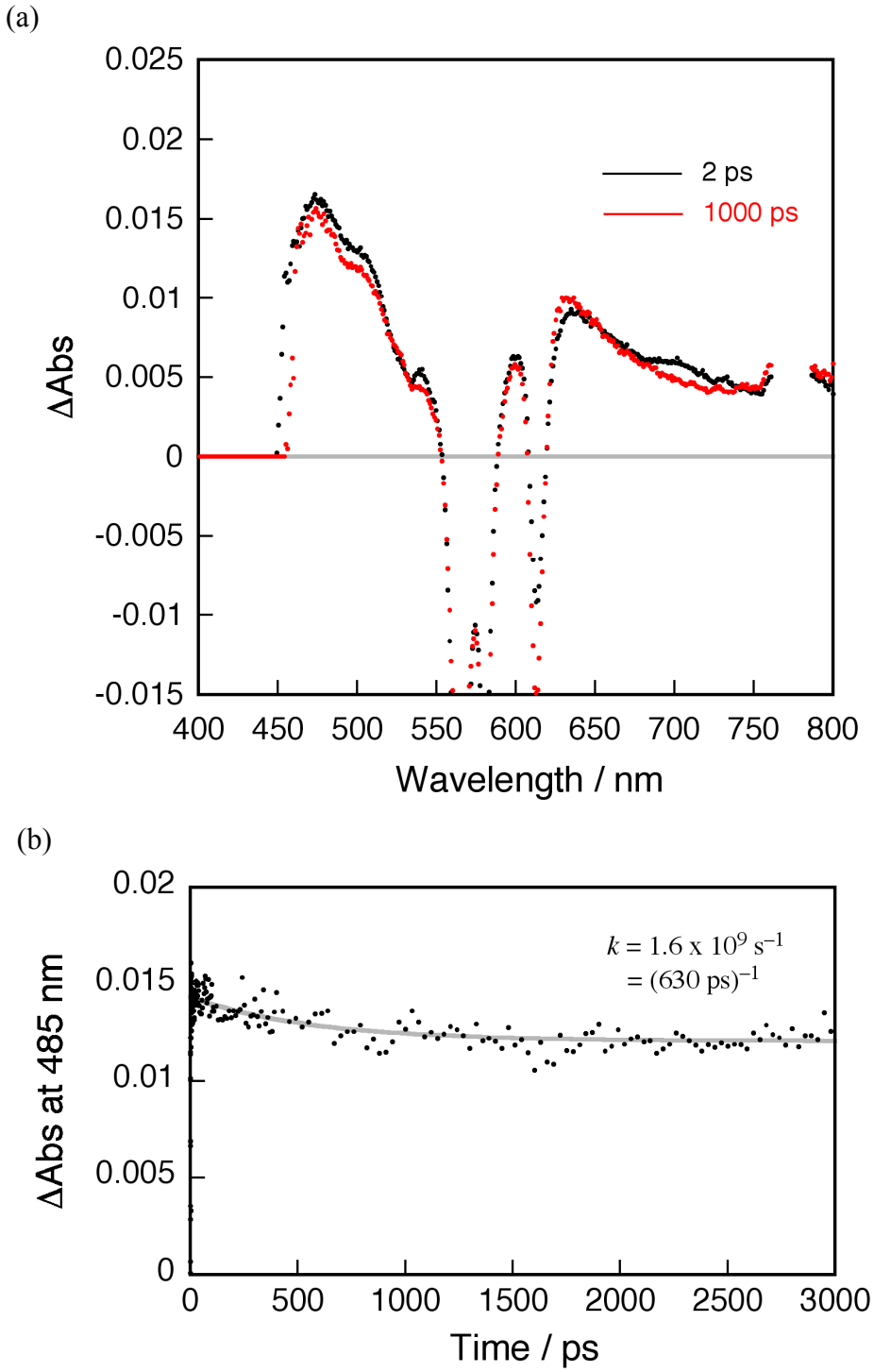
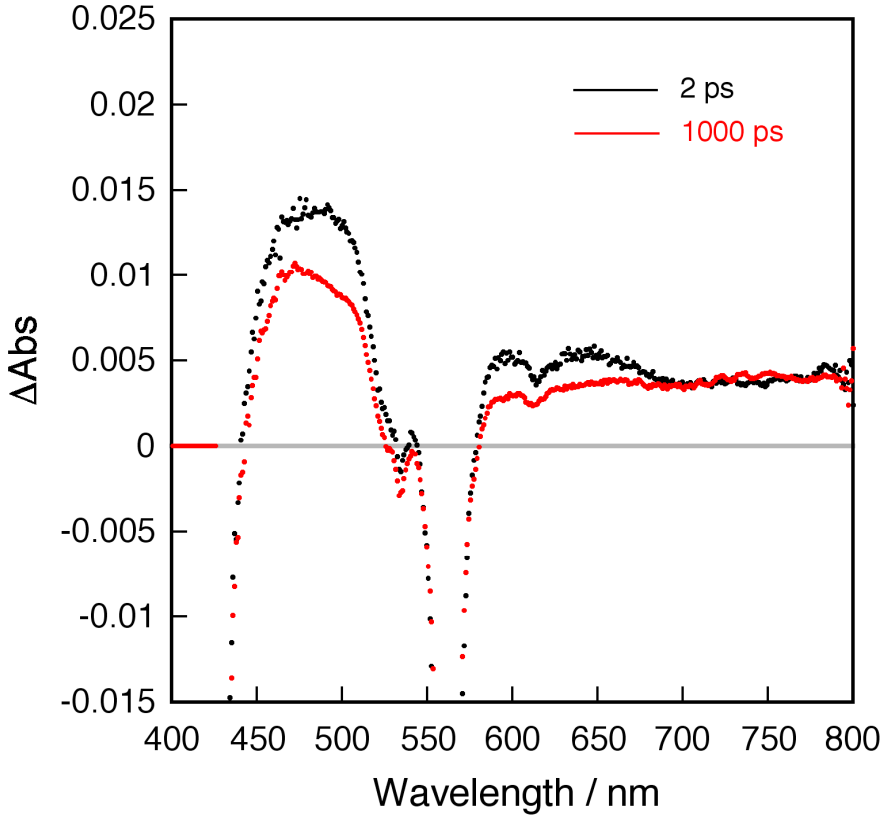


Fig S7 (a)Transient absorption spectra and (b) time profile of **PdP-DK** in toluene taken after femtosecond laser excitation at 410 nm.

(a)



(b)

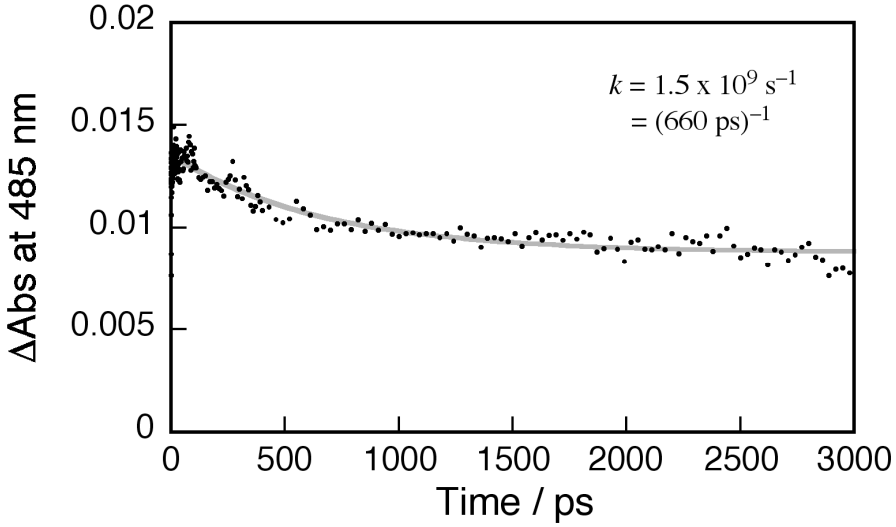


Fig S8 (a) Transient absorption spectra and (b) time profile of **PdP-DOHa** in toluene taken after femtosecond laser excitation at 410 nm.

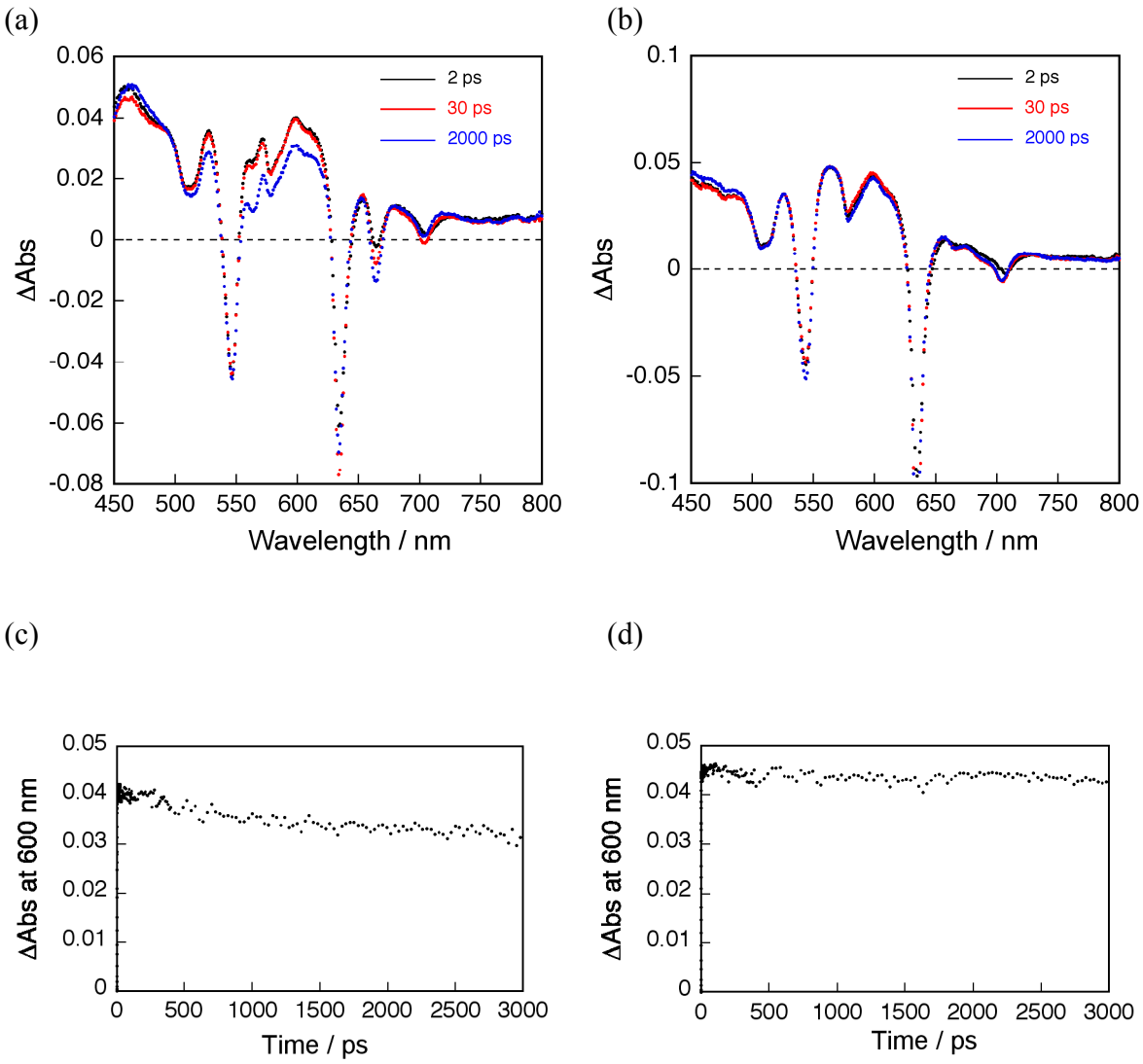


Fig S9 Transient absorption spectra of (a) **H_2P-DK** and (b) **H_2P-DOHa** and time profiles of (c) **H_2P-DK** and (d) **H_2P-DOHa** in toluene. λ_{EX} = 410nm.

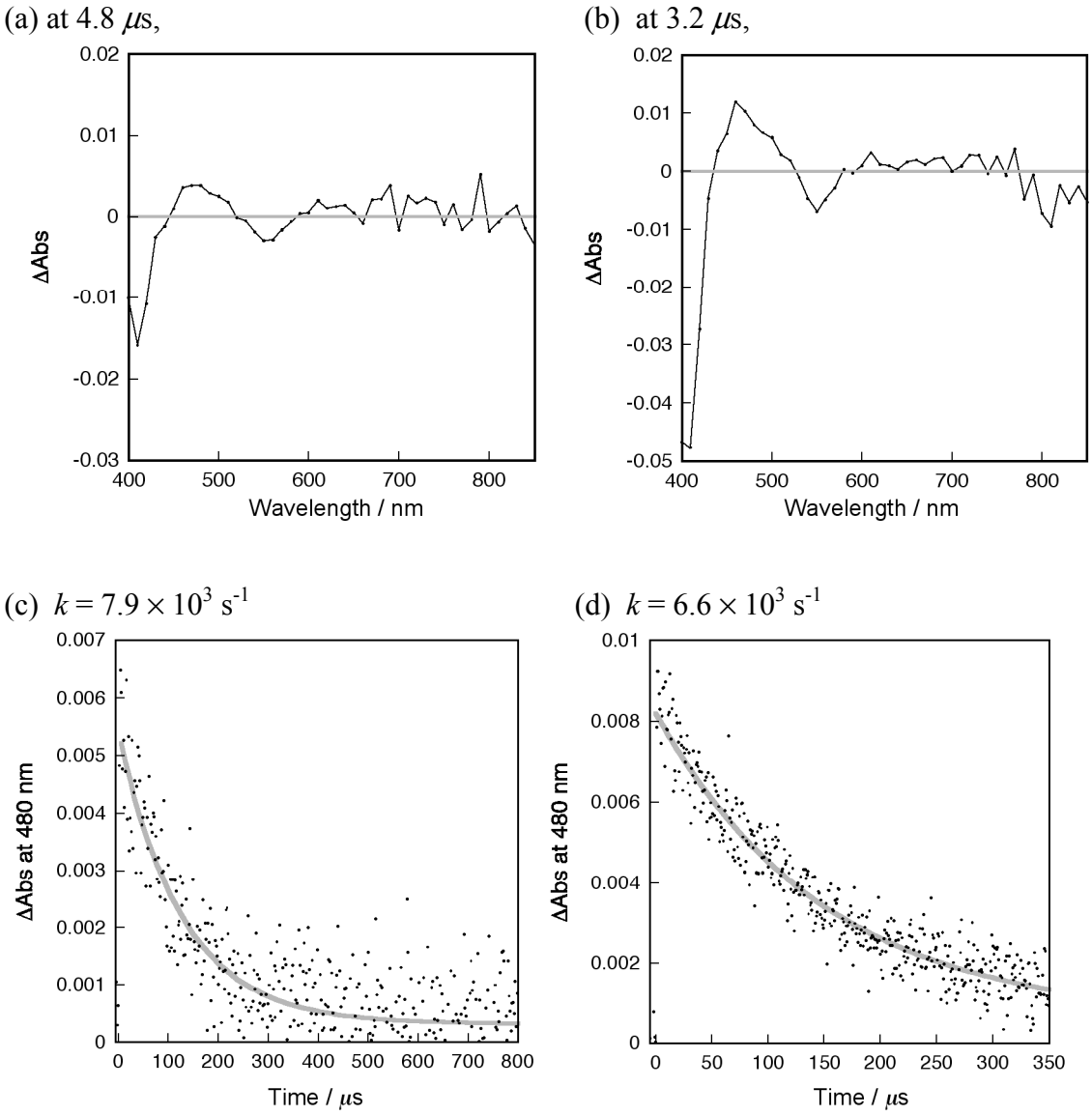
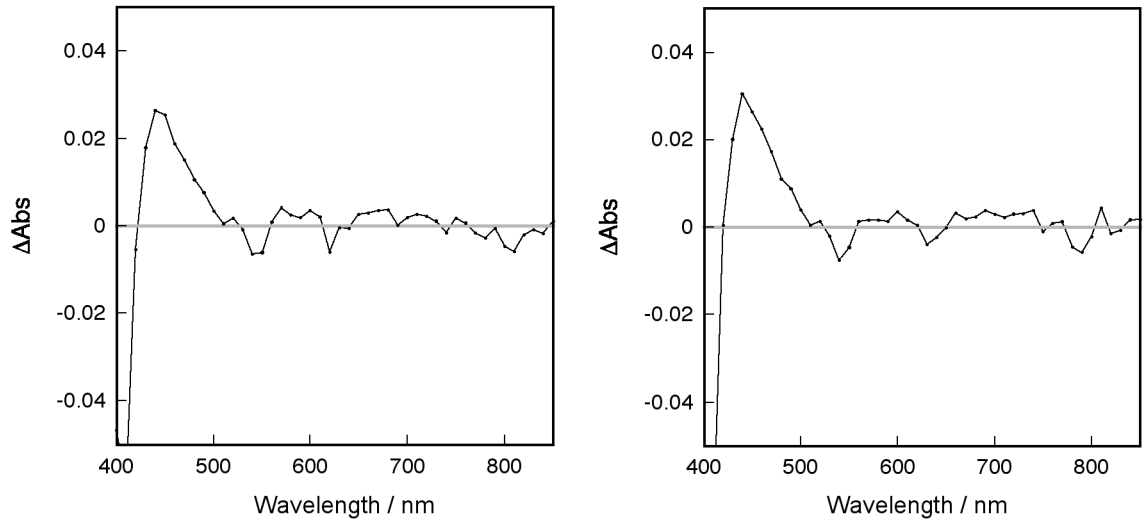


Fig S10 Nanosecond transient absorption spectra of **H_2P-DK** in (a) PhCN at 4.8 μs; (b) toluene at 3.2 μs; and its decay curves in (c) PhCN; (d) toluene; excited by 426 nm laser flash.

(a) at 48 μs, (b) at 18 μs,



(c) $k = 6.1 \times 10^3$ s^{-1} (d) $k = 6.6 \times 10^3$ s^{-1}

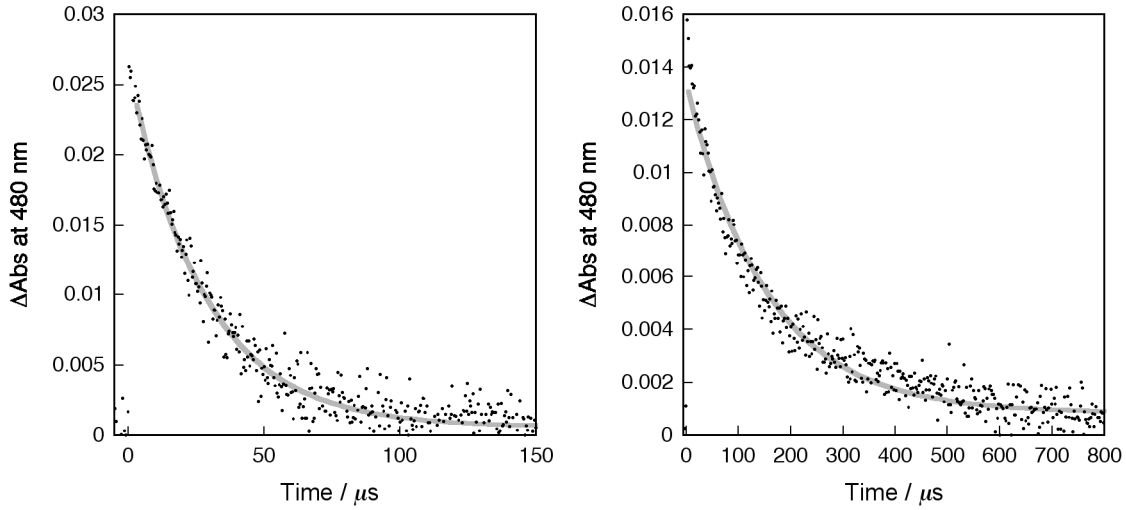
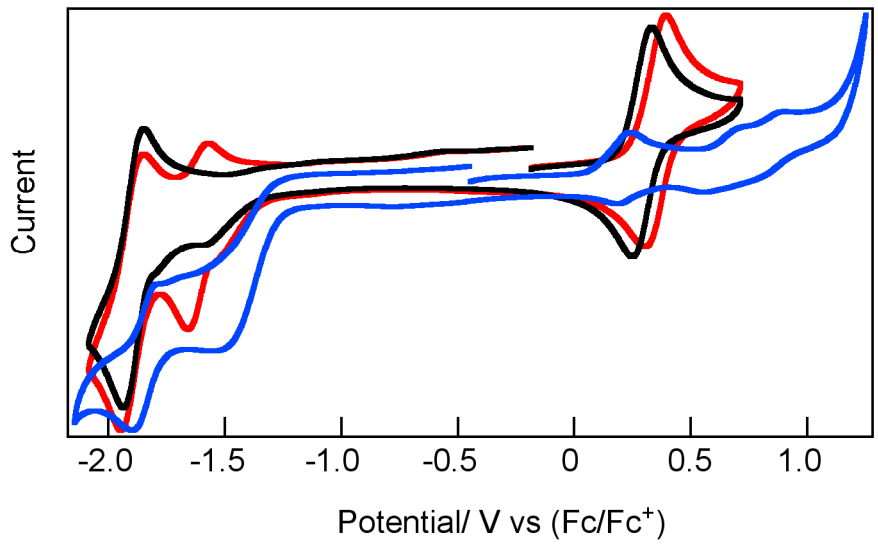


Fig S11 Nanosecond transient absorption spectra of **H_2P-DOHa** in (a) PhCN at 48 μs; (b) toluene at 18 μs; and its decay curves in (c) PhCN; (d) toluene; excited by 426 nm laser flash.

(a)



(b)

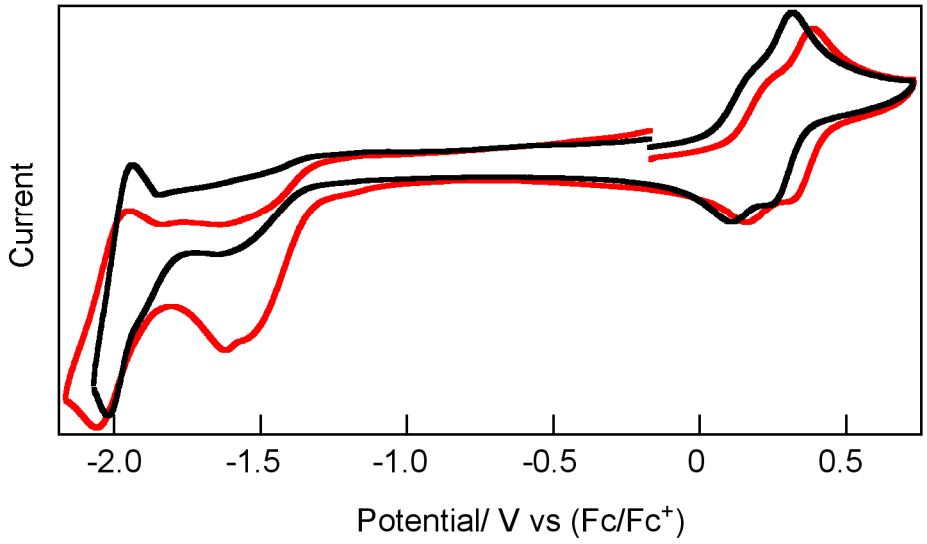


Fig S12 Cyclic voltammograms of (a) **H_2P-DK** (red), **H_2P-DOHa** (black), and **H_2P-mA** (blue), and (b) **PdP-DK** (red) an **PdP-DOHa** (black) in deaerated PhCN containing *n*-Bu_4NPF_6 as a supporting electrolyte at 298 K (100 mV s^{-1}). WE: glassy carbon; CE: Pt; RE: $Ag/AgNO_3$, V vs Fc/Fc^+.

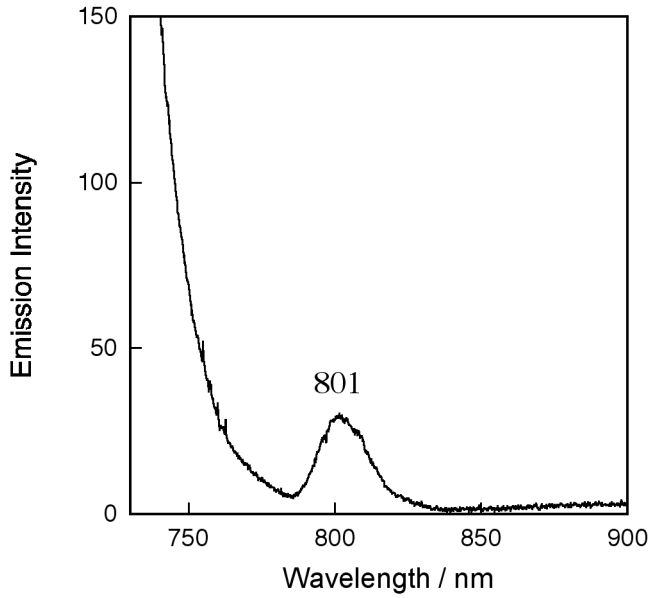


Fig S13 Phosphorescence spectrum of **H_2P-DOHa** in 2-methyltetrahydrofuran glass at 77 K. Excitation wavelength: 574 nm.

Full authors list for ref. 28.

[28] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, H. P. KnoxHratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, R. C.*, Gaussian, Inc., Wallingford CT, 2004.