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SUPPORTING INFORMATION

Realizing Near-Infrared Mechanophosphorescence from Organic Host/Guest System

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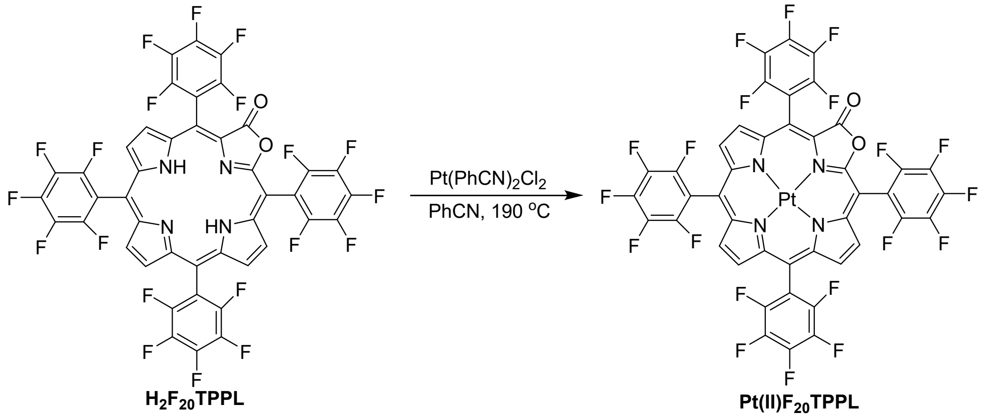
I. Experimental section

1. General Information

The synthetic reactions were performed using the standard Schlenk technique under an argon atmosphere. Reagents were obtained commercially and used without further purification unless indicated otherwise. All solvents used in the reaction were dried and freshly distilled. Flash chromatography was performed using Merck silica gel 60 and a gradient solvent system (CH_2Cl_2/CH_3OH as eluent). H_2F_{20}TPPL was synthesized following literature's procedure. [S1] ^{1}H, ^{19}F, and ^{13}C NMR spectra were measured either on a Varian XL-400 or Bruker AVANCE-500 spectrometer. Mass spectra were determined on a Thermo Scientific Q Exactive HF Orbitrap-FTMS spectrometer. Excitation spectra, photoluminescence(PL) spectra, phosphorescence spectra and phosphorescence lifetimes were measured using an Edinburgh FLS 1000 steady-transient fluorescence spectrophotometer. Mechanoluminescence(ML) spectra was measured on an Ocean Optic QE 65Pro spectrometer with Ocean Optic reflection probes R600-125F. Photos and videos were recorded by Sony LICE-6400M camera and EZVIZ C6CN 1080P camera.

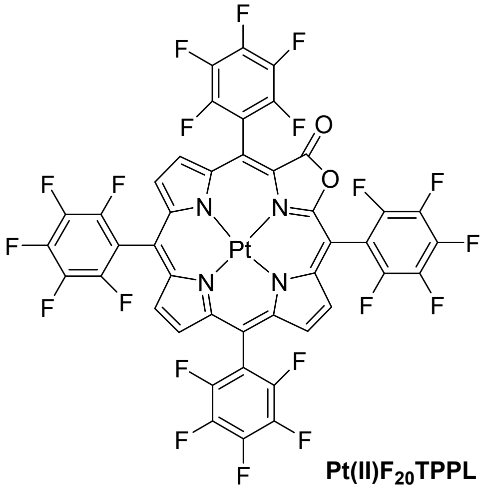
2. The Synthesis of Pt(II)F_{20}TPPL



Scheme S1 Synthetic Procedure for Pt(II)F$_{20}$TPPL.

To a PhCN (20 mL) solution of H$_2$F$_{20}$TPPL (100 mg) was added Pt(PhCN)$_2$Cl$_2$ (2 eq.) under nitrogen. The mixture was heated to 190 °C and stirred for 24 hours. Then the mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was isolated by column chromatography eluted with CH$_2$Cl$_2$/hexane (1:3) to provide Pt(II)F$_{20}$TPPL in a 34 % yield (41 mg).

Characterization data



Pt(II)F$_{20}$TPPL was obtained by flash chromatography on a silica gel column with CH$_2$Cl$_2$/hexane (1:3) as an eluent. Purple-red solid. 41 mg, yield 34 %. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.70 - 8.75 (m, 6H). ^{19}F NMR (376 MHz, CDCl$_3$): δ -136.53 – -136.80 (m, 6F), -138.22 (dd, J = 22.9, 7.2 Hz, 2F), -150.13 – -150.33 (m, 3F), -150.90 (t, J = 20.8 Hz, 1F), -160.40 – -160.68 (m, 6), -161.26 (dt, J = 21.6, 6.8 Hz, 2F). ^{13}C NMR (126 MHz, CDCl$_3$): δ 163.2, 148.7, 146.6, 142.7, 140.9, 139.9, 139.3, 138.7, 133.9, 131.6, 130.3, 130.0, 129.9, 129.0, 118.6, 112.0, 108.4, 105.9, 87.9; all *meso*-aryl carbon atoms are broadened, often beyond distinction, because of F-C couplings. (LR-MALDI-Orbitrap) *m/z* calcd. for $[C_{43}H_6F_{20}N_4O_2Pt]^+$: 1185.0 $[M+H]^+$; found: 1185.0.

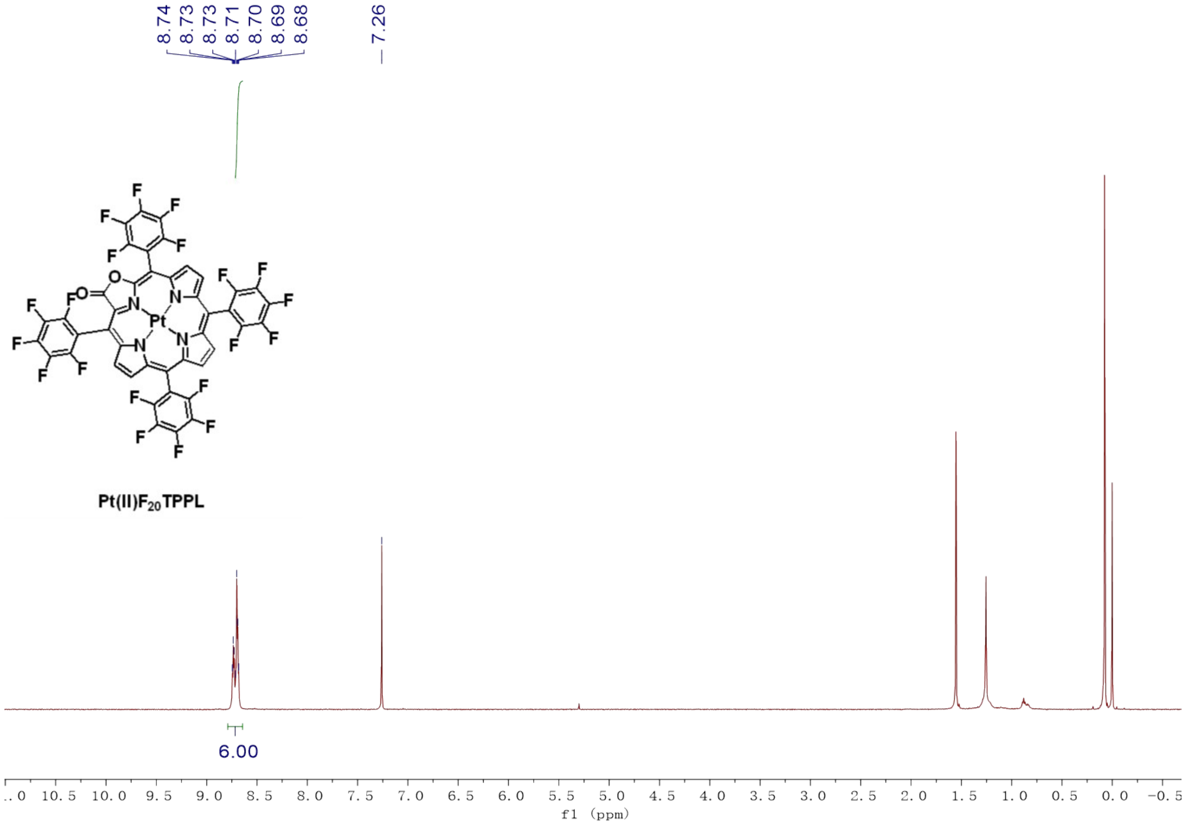


Figure S1. ^{1}H NMR spectrum of Pt(II)F_{20}TPPL in $CDCl_3$. (400 MHz)

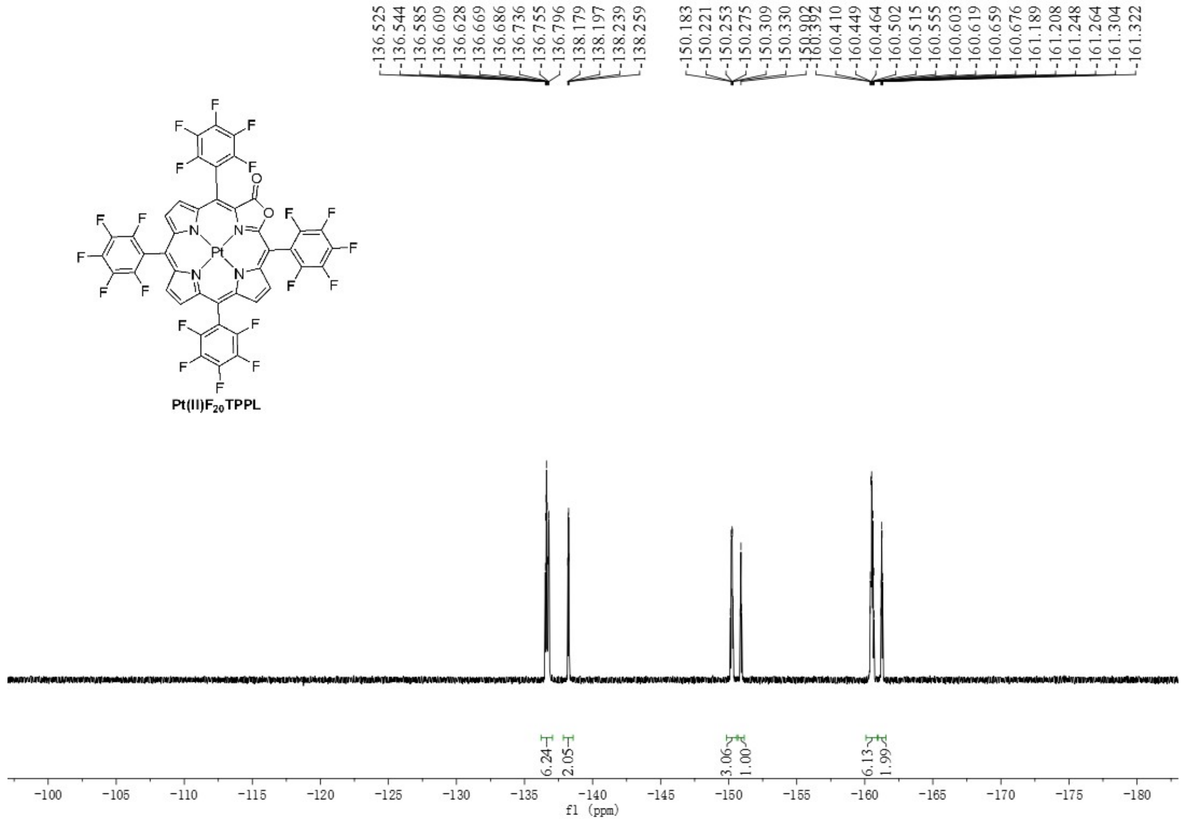


Figure S2. ^{19}F NMR spectrum of Pt(II)F_{20}TPPL in $CDCl_3$. (376 MHz)

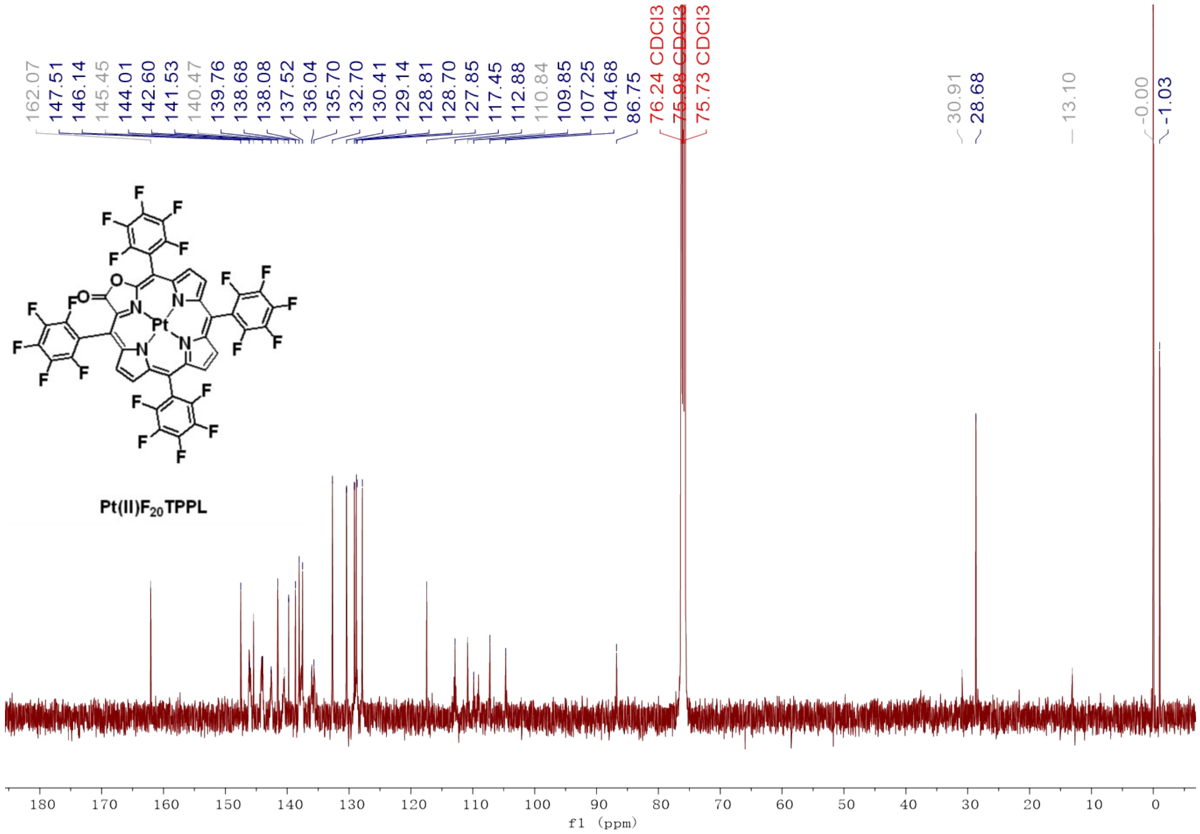


Figure S3. ^{13}C NMR spectrum of Pt(II)F_{20}TPPL in $CDCl_3$. (126 MHz)

3. The Preparation of H/G Doping Systems

0.5% Pt(II)F$_{20}$TPPL/*N*-hexyl Cz: 0.5 g of host matrix (*N*-hexyl Cz) and mixed with the Pt(II)F_{20}TPPL (0.5 % (w/w)) were slightly heated up tothe melt and then cooled down to room temperature for recrystallization.

1.0% Pt(II)F$_{20}$TPPL/*N*-hexyl Cz and 2.0% Pt(II)F$_{20}$TPPL/*N*-hexyl Cz: Following the same synthetic procedure as 0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz.

Fig. The XRD spectra of Pt(II)F_{20}TPPL, N-hexyl carbazole, 0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz, 1.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz and 2.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz.

Fig. The XRD spectra of Pt(II)F_{20}TPPL, N-hexyl carbazole, 0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz, 1.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz and 2.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz.

Fig. The XRD spectra of Pt(II)F_{20}TPPL, N-hexyl carbazole, 0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz, 1.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz and 2.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz.

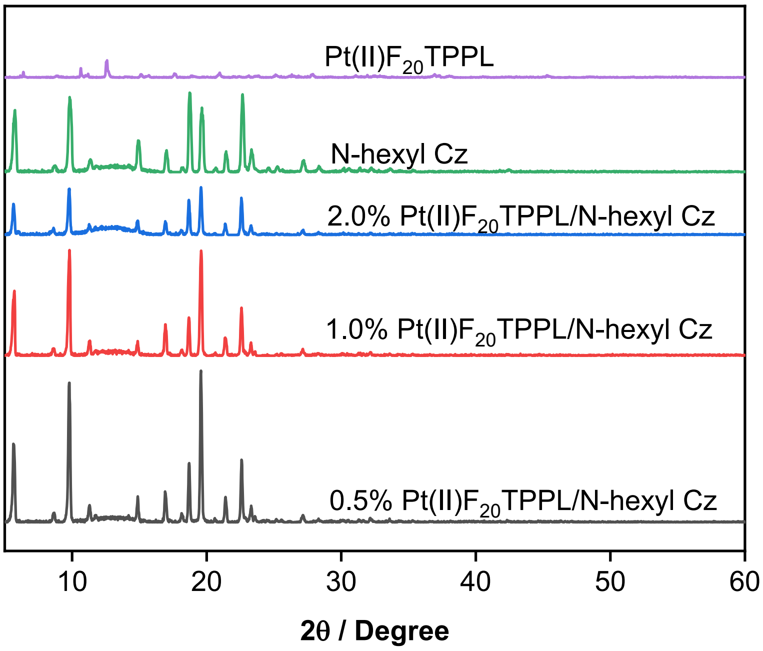


Figure S4. The XRD spectra of Pt(II)F_{20}TPPL, N-hexyl carbazole, 0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz, 1.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz and 2.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz.

4. ML Experiments

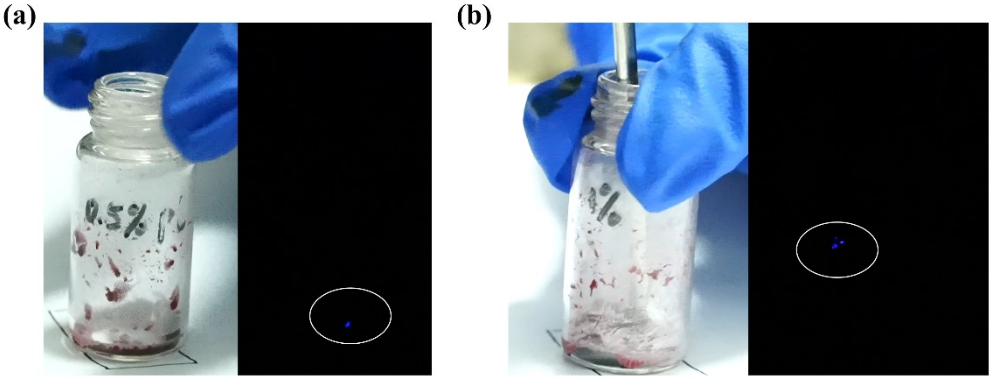


Figure S5. (a) Photographs of 0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz for the ML phenomenon taken in a dark condition. (b) Photographs of 1.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz for the ML phenomenon taken in a dark condition.

5. Time-Resolved Decay Curves

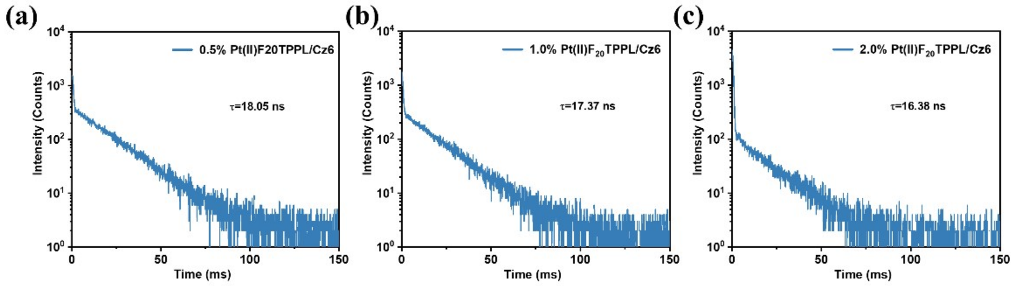


Figure S6. (a) Time-resolved decay curves of 0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz at 409 nm excited at 365 nm. (b) Time-resolved decay curves of 1.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz at 409 nm excited at 365 nm. (c) Time-resolved decay curves of 2.0% Pt(II)F_{20}TPPL/*N*-hexyl Cz at 409 nm excited at 365 nm.

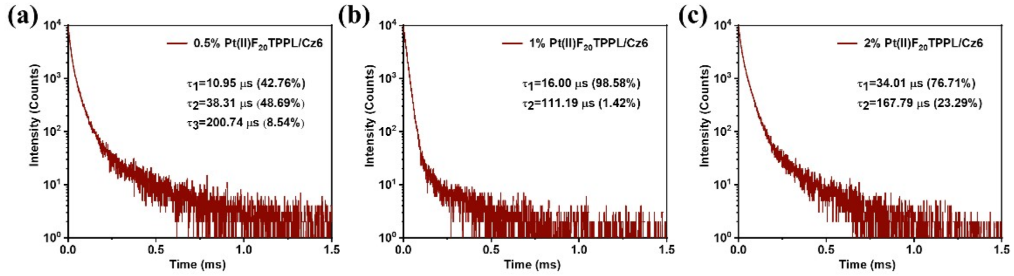


Figure S7. (a) Time-resolved decay curves of 0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz at 746 nm excited at 365 nm. (b) Time-resolved decay curves of 1% Pt(II)F_{20}TPPL/*N*-hexyl Cz at 746 nm excited at 365 nm. (c) Time-resolved decay curves of 2% Pt(II)F_{20}TPPL/*N*-hexyl Cz at 746 nm excited at 365 nm.

6. Photophysical Properties

Table S1. Photophysical properties of powders for Pt(II)F_{20}TPPL, 0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz, 1% Pt(II)F_{20}TPPL/*N*-hexyl Cz, 2% Pt(II)F_{20}TPPL/*N*-hexyl Cz and 2% Pt(II)F_{20}TPPL/*N*-hexyl Cz

Sample	Fluo.		Phos. (at 746 nm)				ML
	λ_{max}(nm)	τ_F(ns)	λ_{max}(nm)	τ_{p1} (μs)	τ_{p2} (μs)	τ_{p3} (μs)	λ_{max} (nm)
Pt(II)F_{20}TPPL	\	\	736, 806	45	\	\	\
0.5% Pt(II)F_{20}TPPL/*N*-hexyl Cz	409	18.05	742	10.95 (42.76%)	38.31 (48.69%)	200.74 (8.54%)	434
1% Pt(II)F_{20}TPPL/*N*-hexyl Cz	409	17.37	744	16.00 (98.58%)	111.19 (1.42%)	\	434,745
2% Pt(II)F_{20}TPPL/*N*-hexyl Cz	409	16.38	746	34.01 (76.71%)	167.79 (23.29%)	\	745

7. Theoretical Calculations

The density functional theory (DFT) method was used to carry out MO and electronic states for ***N*-hexyl Cz** and **Pt(II)F_{20}TPPL** by using PBE0/6-31g* basis sets. All the calculations were performed with the Gaussian 09 D01 program package.[S2]

II. References

[S1] Y. Yu, H. Lv, X. Ke, B. Yang, J.-L. Zhang, Ruthenium-Catalyzed Oxidation of the Porphyrin b,b’-Pyrrolic Ring: A General and Efficient Approach to Porpholactones. *Adv. Synth. Catal.* **2012**, *354*, 3509 – 3516.

[S2] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009