## for

# Oxidation-Induced Detachment of Ruthenoarene Unit and Oxygen Insertion in Bis-Pd(II) Hexaphyrin $\pi$-Ruthenium Complexes 

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Figure S1. ${ }^{1} \mathrm{H}$ and ${ }^{19} \mathrm{~F}$ NMR spectra of 4 in $\mathrm{CDCl}_{3}$ at room temperature. Peak marked with * are due to residual solvents.
${ }^{1} \mathrm{H}$


Figure S2. ${ }^{1} \mathrm{H}$ and ${ }^{19} \mathrm{~F}$ NMR spectra of $\mathbf{6}$ in $\mathrm{CDCl}_{3}$ at room temperature. Peak marked with * are due to residual solvents and impurities.

## 2. HR mass spectra

(a)

(b)


Figure S3. Observed (top) and simulated (bottom) HR APCI-TOF-MS spectra of (a) 4 and (b) 6.

## 3. Absorption spectra



Figure S4. Absorption spectral changes of titration experiments upon addition of TBAH to the solution of 3 in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$.


Figure S5. Absorption spectra of 4 in four solvents indicating almost no solvent polarity effect.


Figure S6. Absorption spectra of $\mathbf{6}$ in five solvents indicating almost no solvent polarity effect.

## 4. Electrochemical properties

(a)

(b)


Figure S7. Cyclic voltammograms of (a) 4, and (b) 6. Differential pulse voltammograms of 7 and are also shown. Measurement conditions: solvent: $\mathrm{CH}_{2} \mathrm{Cl}_{2}$; scan rate: $0.05 \mathrm{~V} / \mathrm{s}$; working electrode: Pt ; reference electrode: $\mathrm{Ag} / \mathrm{AgNO}_{3}$; counter electrode: Pt; electrolyte: $0.1 \mathrm{M} n \mathrm{Bu}_{4} \mathrm{NPF}_{6}$.

## 5. Crystallographic data

a)

b)

c)


Figure S8. X-Ray crystal structure of 4 (a) top view, (b) perspective view, and (c) packing view. The thermal ellipsoids are $50 \%$ probability. For (a) and (b), one of two independent molecules is shown. Solvent molecules, pentafluorophenyl group (perspective and packing view) and hydrogen atoms are omitted for clarity.
a)

b)



Figure S9. X-Ray crystal structure of 6 (a) top view, (b) side view, and (c) perspective view. The thermal ellipsoids are $50 \%$ probability. Solvent molecules, pentafluorophenyl group (side and perspective view) and hydrogen atoms except for NHs are omitted for clarity.

|  | 4 | 6 |
| :---: | :---: | :---: |
| formula | 2(C76 $\left.{ }^{( } \mathrm{H}_{2} \mathrm{~F}_{30} \mathrm{~N}_{6} \mathrm{Pd}_{2} \mathrm{Ru}\right), 2\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right), \mathrm{C}_{6} \mathrm{H}_{14}$ | $\mathrm{C}_{86} \mathrm{H}_{36} \mathrm{~F}_{30} \mathrm{~N}_{6} \mathrm{OPd}_{2} \mathrm{Ru}_{2}, 1.45\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$, $2(\mathrm{CO})$ |
| solvent | $\mathrm{CH}_{2} \mathrm{Cl}_{2} / n$-hexane | $\mathrm{CH}_{2} \mathrm{Cl}_{2} / \mathrm{MeOH}, \mathrm{H}_{2} \mathrm{O}$ |
| $M_{r}$ | 4061.76 | 2333.14 |
| T[K] | 93 | 93 |
| crystal system | orthorhombic | monoclinic |
| space group | P21 2121 (No.19) | P2 $1^{\prime} \mathrm{C}$ (No.14) |
| $a[\AA]$ | 19.7984(1) | 17.9085(1) |
| $b[\AA]$ | 26.4804(1) | 17.8783(2) |
| $c[A ̊]$ | 27.2848(1) | 26.0682(2) |
| $\alpha\left[{ }^{\circ}\right]$ | 90 | 90 |
| $\beta$ [ ${ }^{\circ}$ ] | 90 | 103.841(1) |
| $\gamma\left[{ }^{\circ}\right]$ | 90 | 90 |
| $V\left[\AA^{3}\right]$ | 14304.59(10) | 8103.99(12) |
| Z | 4 | 4 |
| $\rho_{\text {calcd }}\left[\mathrm{g} / \mathrm{cm}^{3}\right]$ | 1.886 | 1.912 |
| $R_{1}[I>2 \sigma(I)]$ | 0.0513 | 0.0347 |
| $\mathrm{w} R_{2}$ (all data) | 0.1470 | 0.0980 |
| GOF [ $I>2 \sigma(I)]$ | 1.049 | 1.064 |
| CCDC No. | 2005822 | 2005823 |

Table S1. Bond lengths (X-ray and DFT calculation) and bond order (DFT) of 4.

|  | Bond length (X-ray) $[\AA ̊]$ | Bond length (DFT) $[\AA ̊]$ | Bond order (DFT) |
| :---: | :---: | :---: | :---: |
| Pd1-C1 | $1.988(9)$ | 2.015 | 0.5979 |
| Pd1-C4 | $2.014(9)$ | 2.031 | 0.5544 |
| Pd1-Ru1 | $2.8269(8)$ | 2.878 | 0.1956 |
| Pd2-C2 | $2.002(9)$ | 2.026 | 0.5652 |
| Pd2-C3 | $1.996(8)$ | 2.009 | 0.6045 |
| Pd2-Ru1 | $2.8417(8)$ | 2.937 | 0.1883 |
| C1-C2 | $1.410(13)$ | 1.394 | 1.4605 |
| C1-Ru1 | $2.306(8)$ | 2.367 | 0.3532 |
| C2-Ru1 | $2.219(8)$ | 2.301 | 0.4032 |
| C3-C4 | $1.380(13)$ | 1.394 | 1.4628 |
| C3-Ru1 | $2.348(8)$ | 2.420 | 0.3274 |
| C4-Ru1 | $2.215(8)$ | 2.286 | 0.4224 |



Table S2. Bond lengths (X-ray and DFT calculation) and bond order (DFT) of 6.

|  | Bond length (X-ray) $[\AA ̊]$ | Bond length (DFT) $[\AA]]$ | Bond order (DFT) |
| :---: | :---: | :---: | :---: |
| Pd1-C1 | $2.552(3)$ | 2.591 | 0.1179 |
| Pd1-C4 | $2.057(3)$ | 2.080 | 0.4421 |
| Pd1-O1 | $2.014(2)$ | 2.039 | 0.2628 |
| Pd1-Ru1 | $2.9548(5)$ | 2.947 | 0.2351 |
| Pd1-Ru2 | $2.9651(6)$ | 3.035 | 0.2453 |
| Pd2-C2 | $1.961(3)$ | 1.980 | 0.5061 |
| Pd2-C3 | $2.099(3)$ | 2.134 | 0.4516 |
| Pd2-Ru1 | $3.1146(6)$ | 3.216 | 0.2357 |
| Pd2-Ru2 | $2.8568(5)$ | 2.866 | 0.2848 |
| C1-C2 | $1.404(4)$ | 1.410 | 1.1260 |
| C1-O1 | $1.355(4)$ | 1.337 | 0.8766 |
| C1-Ru1 | $3.036(3)$ | 3.102 | 0.0109 |
| C1-Ru2 | $2.396(4)$ | 2.507 | 0.3298 |
| C2-Ru1 | $3.367(3)$ | 3.483 | 0.0562 |
| C2-Ru2 | $2.250(4)$ | 2.249 | 0.4557 |
| C3-C4 | $1.478(4)$ | 1.464 | 1.0713 |
| C3-Ru1 | $2.179(3)$ | 2.179 | 0.4825 |
| C3-Ru2 | $2.263(3)$ | 2.402 | 0.4331 |
| C4-Ru1 | $2.242(3)$ | 2.314 | 0.4285 |
| C4-Ru2 | $2.239(3)$ | 2.296 | 0.4366 |
| Ru1-O1 | $2.120(2)$ | 2.145 | 0.4018 |


6. Resonance contributors and HOSE values
(a)


$26 \pi$ system
$26 \pi$ system
(b)


Scheme S1. Plausible resonance contributors of hexaphyrin ligands of (a) 4 and (b) 3. Effective $\pi$ conjugated structures are indicated in bold lines. meso-Pentafluorophenyl groups are omitted for clarity.


6A
$26 \pi$ systems


6C


6D
$26 \pi$ system

6B
$26 \pi$ systems


$26 \pi$ system




6E
$28 \pi$ system


6F
$28 \pi$ system

Scheme S2. Plausible resonance contributor of hexaphyrin ligands of 6 . Effective $\pi$-conjugated structures are indicated in bold lines. meso-Pentafluorophenyl groups are omitted for clarity.

## HOSE calculation ${ }^{[13]}$

For the calculation of HOSE, the lengths of $\pi$ bonds in the real molecule were used for the lengths given in the X-ray crystal structures and optimized structures of $\mathbf{4}$ (for the dianion) and $\mathbf{3}$ (for the tetraanion).

Table S3. Harmonic oscillator stabilization energies (HOSE ${ }_{i,}$ kcal $/ \mathrm{mol}$ ) and estimated weights ( $C_{i}$ ) for canonical structures 4A, 4B, 4A', 4B', 3A, 3B, and 3C.

|  | $\operatorname{HOSE}_{i}$ (X-ray) | $C_{i}($ X-ray $)$ | HOSE $_{i}(\mathrm{DFT})$ | $C_{i}$ (DFT) |
| :---: | :---: | :---: | :---: | :---: |
| 4A | 430 | 0.481 | 382 | 0.484 |
| 4B | 399 | 0.519 | 358 | 0.516 |
| $\mathbf{4 A}^{\prime}$ | 508 | - | 453 | - |
| 4B $^{\prime}$ | 476 | - | 430 | - |
| 3A | 427 | 0.342 | 444 | 0.331 |
| 3B | 437 | 0.334 | 446 | 0.329 |
| 3C | 449 | 0.325 | 432 | 0.340 |

Since $\mathbf{4 A}$ and $4 A^{\prime}, \mathbf{4 B}$ and $\mathbf{4 B ^ { \prime }}$ have same structure with different conjugated macrocycles, $4 A^{\prime}$ and $4 \mathbf{B}^{\prime}$ are not considered for estimated weights ( $C_{i}$ ).

Table S4. Harmonic oscillator stabilization energies (HOSE ${ }_{i}, \mathrm{kcal} / \mathrm{mol}$ ) and estimated weights ( $C_{i}$ ) for canonical structures 6A to 6F.

|  | $\operatorname{HOSE}_{i}(\mathrm{X}$-ray $)$ | $C_{i}(\mathrm{X}$-ray $)$ | $\operatorname{HOSE}_{i}(\mathrm{DFT})$ | $C_{i}(\mathrm{DFT})$ |
| :---: | :---: | :---: | :---: | :---: |
| 6A | 312 | 0.189 | 309 | 0.189 |
| 6B | 322 | 0.182 | 315 | 0.185 |
| 6C | 350 | 0.168 | 344 | 0.169 |
| 6D | 362 | 0.162 | 355 | 0.164 |
| 6E | 388 | 0.152 | 389 | 0.149 |
| 6F | 401 | 0.147 | 402 | 0.145 |

Harmonic oscillator stabilization energies were calculated using the method of Krygowski et al. using the original parameterization; estimated weights ( $C_{i}$ ) were calculated according to the formula

$$
C_{i}=\frac{\left(\operatorname{HOSE}_{i}\right)^{-1}}{\sum_{j}\left(\operatorname{HOSE}_{j}\right)^{-1}}
$$

## 7. DFT calculations

All calculations were carried out using the Gaussian 16 program. ${ }^{[52]}$ All structures were fully optimized without any symmetry restriction. The calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional) level, employing a basis set 6-31G(d) for C, $\mathrm{H}, \mathrm{N}, \mathrm{O}, \mathrm{F}$ and LANL2DZ for Pd, Ru. The NICS values and absolute ${ }^{1} \mathrm{H}$ shielding values were obtained with the GIAO method at the B3LYP level, employing a basis set 6-31G(d) for C, H, N, O, F and LANL2DZ for Pd, Ru. The global ring centers for the NICS values were designated at the nonweighted means of the carbon and nitrogen coordinates on the peripheral positions of conjugated macrocycles. In addition, NICS values were also calculated on centers of other local cyclic structures as depicted in the figures. The anisotropy of the induced current density (ACID) calculation was conducted with the CSGT method. ${ }^{[53]}$ The bond order was conducted with the NBO program. ${ }^{[54]}$ Oscillator strengths were calculated with the TD-SCF method at the B3LYP level.


Figure S10. Kohn-Sham orbital diagrams of 4.


Figure S11. Kohn-Sham orbital diagrams of 6 .


Figure S12. Calculated absorption spectrum of 3 on the basis of optimized structure (red bar), observed absorption spectrum (blue line). Selected oscillator strengths: $f=0.0001$ (1011 nm), 0.0505 $(904 \mathrm{~nm}), 0.2581(661 \mathrm{~nm}), 0.1880(554 \mathrm{~nm}), 0.5017(486 \mathrm{~nm}), 0.1846(427 \mathrm{~nm})$, and $0.2712(404 \mathrm{~nm})$.


Figure S13. Calculated absorption spectrum of 4 on the basis of optimized structure (red bar), observed absorption spectrum (blue line). Selected oscillator strengths: $f=0.0166$ (1479 nm), 0.0025 $(1146 \mathrm{~nm}), 0.1084(795 \mathrm{~nm}), 0.1358(599 \mathrm{~nm}), 0.1377(577 \mathrm{~nm}), 0.3587(515 \mathrm{~nm})$, and $0.2791(506 \mathrm{~nm})$.


Figure S14. Calculated absorption spectrum of 6 on the basis of optimized structure (red bar), observed absorption spectrum (blue line). Selected oscillator strengths: $f=0.0049$ ( 1074 nm ), 0.0235 $(851 \mathrm{~nm}), 0.2755(590 \mathrm{~nm}), 0.3568(433 \mathrm{~nm})$, and $0.1830(417 \mathrm{~nm})$.


Figure S15. ACID isosurface of 4 at isovalue of 0.05 . The external magnetic field was applied in the direction from back of the paper to the surface. The current density vectors plotted onto the ACID isosurface indicate the diatropic ring current.


Figure S16. ACID isosurface of $\mathbf{6}$ at isovalue of 0.05 . The external magnetic field was applied in the direction from back of the paper to the surface. The current density vectors plotted onto the ACID isosurface indicate no macrocyclic ring current.


| position | NICS (ppm) |
| :---: | :---: |
| 1 | -2.77 |
| 2 | -20.45 |
| 3 | -12.47 |
| 4 | -17.93 |
| 5 | -3.73 |
| 6 | -22.20 |
| 7 | -2.94 |
| 8 | -18.04 |
| 9 | -11.82 |
| 10 | -19.86 |
| 11 | -3.56 |
| 12 | -18.63 |
| 13 | -24.74 |

Figure S17. NICS(0) values at selected points of 4.


Figure S18. NICS(0) values at selected points of 6 .


Figure S19. Three-dimensional molecular electrostatic potential $\left(-0.035 \mathrm{e}^{\AA} \AA^{-3}\right.$, red and $0.110 \mathrm{e} \AA^{-3}$, blue) mapped on the surface of total electron density $\left(-0.01 \mathrm{e} \AA^{-3}\right)$ for 3 .


Figure S20. Three-dimensional molecular electrostatic potential ( $-0.035 \mathrm{e} \AA^{-3}$, red and $0.110 \mathrm{e}^{\AA} \AA^{-3}$, blue) mapped on the surface of total electron density $\left(-0.01 \mathrm{e} \AA^{-3}\right)$ for 4 .


Figure S21. Three-dimensional molecular electrostatic potential $\left(-0.035 \mathrm{e}^{\AA} \AA^{-3}\right.$, red and $0.110 \mathrm{e} \AA^{-3}$, blue) mapped on the surface of total electron density $\left(-0.01 \mathrm{e} \AA^{-3}\right)$ for 6 .

## 8. References

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