

SUPPORTING INFORMATION

Title: Alkane Oxidation via Photochemical Excitation of a Self-Assembled Molecular Cage

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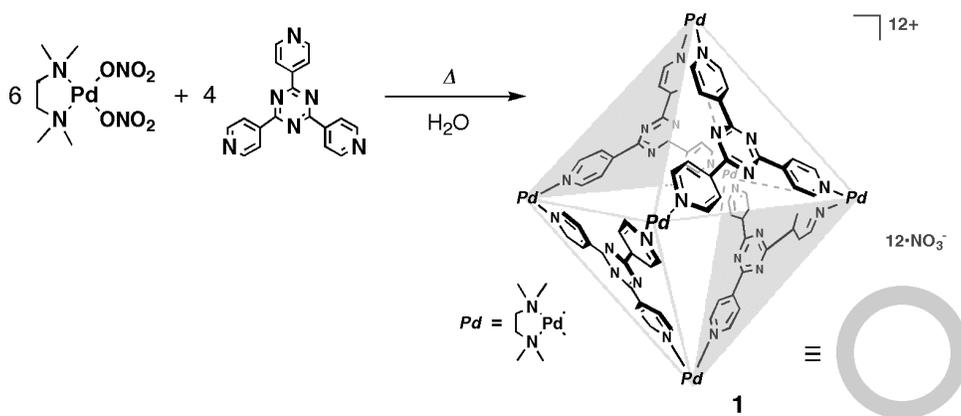
Materials and instrumentations.

^1H , ^{13}C NMR, and other 2D NMR spectra were recorded on Bruker DRX-500 (500 MHz) spectrometer. TMS (CDCl_3 solution) in a capillary served as external standard (δ 0 ppm). IR measurements were carried out as KBr pellets using a DIGILAB FTS2000S instrument. MS (EI) measurements were recorded on a SHIMADZU GCMS-QP5050A. ESR spectra were recorded on JEOL JES-RE1X spectrometer. Photo irradiation was carried out with a SEN LIGHTS CORP. HB400X-15 400-W high-pressure mercury lamp. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Aldrich chemical., Ltd. Deuterated solvents were acquired from Cambridge Isotope Laboratories, Inc. and used as such for the complexation reactions and NMR measurements.

Self-assembly of a coordination cage 1.

2,4,6-tris(4-pyridyl)-1,3,5-triazine (624 mg; 2.00 mmol) was suspended in an aqueous solution (50.0 ml) of (tetramethylethylenediamine) $\text{Pd}(\text{NO}_3)_2$ (1.040 g; 3.00 mmol) and the mixture was stirred at 80 °C for 1 h. The solution was filtered and evaporated to dryness. The residue was recrystallized from a small amount of water to give cage 1 as a pale yellow powder (1.660 g; 0.497 mmol) in 99.5% yield.

(Ref. M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi, K. Ogura, *Nature*, **378**, 469 (1995)).



Typical procedure of the photochemical oxidation of adamantane within **1**.

To a D₂O solution (1.0 mL) of **1** (16.6 mg, 5.0 × 10⁻³ mmol, 5.0 mM), excess amount of adamantane (**2**; ca. 15 mg, 1.1 × 10⁻⁴ mmol) was suspended and the mixture was stirred for 30 min at 60 °C. After filtration, the resulting colorless clear solution was placed in a Pyrex tube and then irradiated for 30 min at room temperature. ¹H-NMR measurement of the D₂O solution was indicated the formation of 1-adamantane-hydroperoxide and 1-adamantanol in 96% total yield (based on **1**), which were assigned by ¹H-NMR and GC-MS analyses after being extracted with CDCl₃.

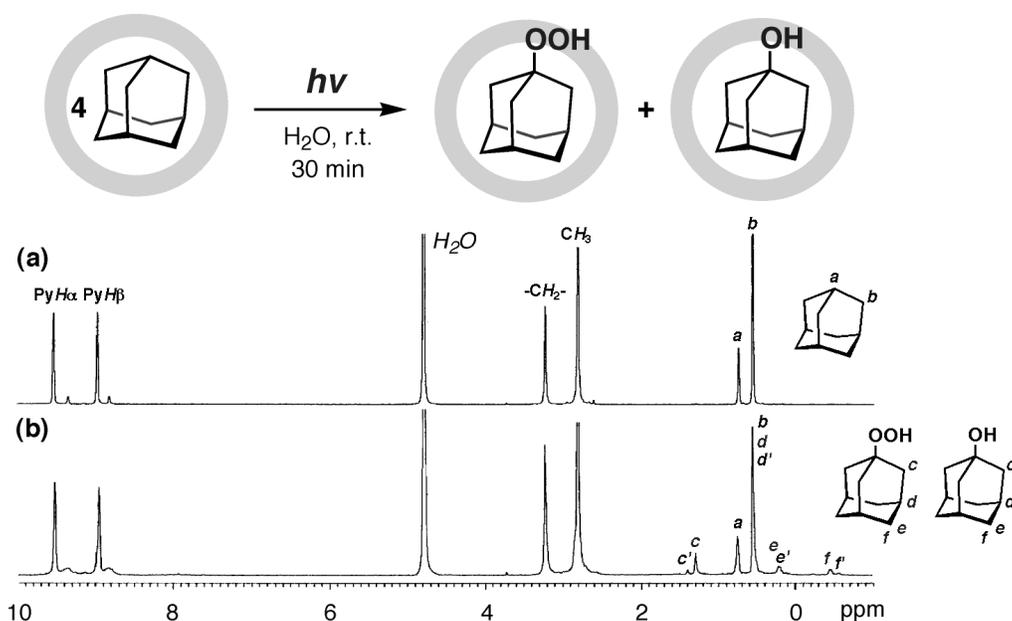


Figure. S1. NMR observation of the photooxidation of adamantane (**2**) within cage **1** (500 MHz, r.t., D₂O, TMS as external standard). (a) An aqueous solution of **1**⊃(**2**)₄ and (b) the reaction mixture after irradiation for 30 min under air.

Physical data of **1**⊃(**2**)₄ before photo irradiation:

¹H-NMR (500 MHz, D₂O, 27 °C, TMS as external standard): δ 9.51 (d, *J* = 5.5 Hz, 24H, PyH_α), 8.94 (d, *J* = 5.5 Hz, 24H, PyH_β), 3.22 (s, 24H, -CH₂-), 2.80 (s, 72H, CH₃), 0.74 (s, 16H, Adamantane CH), 0.55 (s, 48H, Adamantane CH₂). IR (ATR, cm⁻¹): ν 3426 (br), 3102, 2902, 2840, 1619, 1576, 1520, 1471, 1334, 1306, 1236, 1210, 1059, 1007, 955, 877, 814.

Physical data of 1 \Rightarrow (2)₄ after photo irradiation:

¹H-NMR (500 MHz, D₂O, 27 °C, TMS as external standard): δ 9.51 (s, 24H, PyH _{α}), 8.95 (s, 24H, PyH _{β}), 3.21 (s, 24H, -CH₂-), 2.79 (s, 72H, CH₃), 1.38 (s, 1-AdOH), 1.28 (s, 1-AdOOH), 0.74 (s, Adamantane CH), 0.54 (s, Adamantane CH₂, 1-AdOH, and 1-AdOOH), 0.17 (d, J = 11.7 Hz, 1-AdOH and 1-AdOOH), -0.46 (d, J = 11.8 Hz, 1-AdOOH), -0.57 (br, 1-AdOH). IR (ATR, cm⁻¹): ν 3431 (br), 3102, 2906, 2844, 1619, 1575, 1521, 1470, 1360, 1316, 1279, 1237, 1062, 1042, 1007, 955, 876, 813.

¹H-NMR (500 MHz, CDCl₃, 27 °C, TMS as external standard, after extraction): δ 7.12 (s, 1H, 1-AdOOH), 2.19 (br, 3H, 1-AdOOH), 2.15 (s, 3H, 1-AdOH), 1.878 (s, 4H, AdH), 1.81 (s, 6H, 1-AdOOH), 1.75 (s, 12H, AdH), 1.72 (s, 6H, 1-AdOH), 1.66-1.63 (m, 1-AdOOH and 1-AdOH), 1.30 (s, 1H, 1-AdOH). ¹³C-NMR (125 MHz, CDCl₃, 27 °C, TMS as external standard, after extraction): δ 80.1 (C_q, 1-AdOOH), 68.2 (C_q, 1-AdOH), 45.4 (CH₂, 1-AdOH), 39.7 (CH₂, 1-AdOOH), 37.8 (CH₂, AdH), 36.4 (CH₂, 1-AdOOH), 36.1 (CH₂, 1-AdOH), 30.6 (CH, 1-AdOH), 30.4 (CH, 1-AdOOH), 28.4 (CH, AdH). IR (ATR, cm⁻¹): ν 2897, 2847, 2667, 1726, 1580, 1514, 1448, 1368, 1352, 1101, 964.

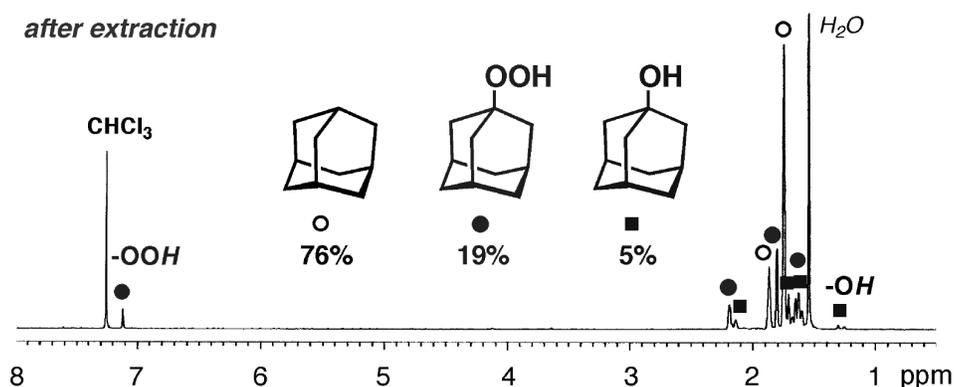


Figure S2. ¹H-NMR observation of photo-oxidized products after extraction with CDCl₃ (500 MHz, r.t., CDCl₃, TMS as external standard).

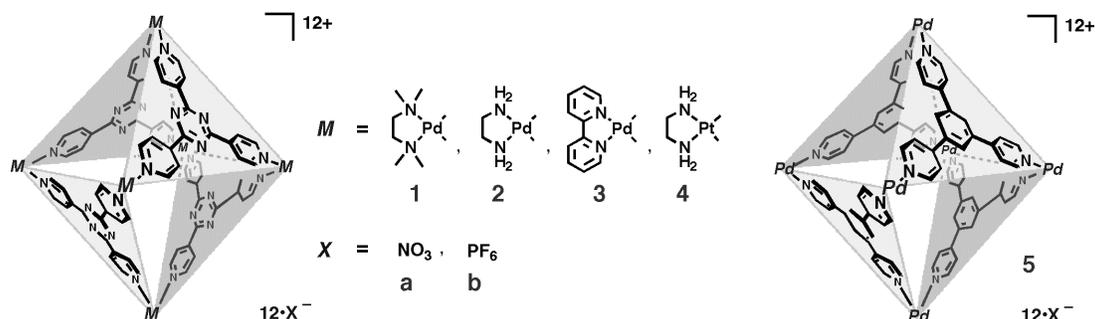
Table S1. Color, UV-vis, and ESR data of Cage \supset (G)_n after the photo-irradiation.

Cage \supset (G) ₄ (G=Adamantane)	Solvent	Temp.	Color	UV-vis ^{*1}	ESR ^{*2}
1a	H ₂ O	r.t.	blue	593(9300), 744(3600)	2.003
	H ₂ O	-170 °C	blue	————	2.002
	powder	r.t.	deep-blue	————	2.002
	powder	-170 °C	deep-blue	————	2.002
1b	MeCN	r.t.	blue	605(8500), 744(4800)	2.002
		-170 °C	blue	————	2.002
2a	H ₂ O	r.t.	blue	573(3600), 718(1200)	2.003
		-170 °C	blue	————	2.003
3a	H ₂ O	r.t.	blue- green	616(1900), 756(1100)	2.003
4a	H ₂ O	r.t.	blue	592(1000) ^{*3}	2.003

Cage \supset (G) _n	Solvent	Temp.	Color	UV-vis	ESR
1a	H ₂ O	r.t.	blue	577(11000), 680(7400)	2.003 ^{*4}
1b (G=Cyclooctane)	MeCN	r.t.	blue	————	2.002
1a (G=Cycloheptane)	H ₂ O	r.t.	blue	577(6600), 677(4600)	2.003 ^{*4}
1a (G=Cyclohexane)	H ₂ O	r.t.	blue	587(4800), 720(3000)	2.003 ^{*4}
1a	H ₂ O	r.t.	n.r.	n.r.	silent
1b (G = none)	MeCN	r.t.	n.r.	n.r.	silent

Cage \supset (G) _n	Solvent	Temp.	Color	UV-vis	ESR
5a	H ₂ O	r.t.	n.r.	n.r.	silent
5b	MeCN	r.t.	n.r.	n.r.	silent

(G=Cyclooctane)



Conditions: After photo-irradiation of the H₂O or MeCN solution of Cage \supset (G)_n for 30 min under argon, UV-vis (2.0 mM, 1.0 mm quartz cell) and ESR (5.0 mM, quartz tube or capillary) spectra were measured at r.t. or -170 °C. n.r. = no reaction and no change. ^{*1} Molar absorption coefficients (ϵ , M⁻¹cm⁻¹) were determined based on M₆L₄ \supset (G)_n complex. ^{*2} g values were based on MnO as external standard. ^{*3} 4.0 mM. ^{*4} -266 °C

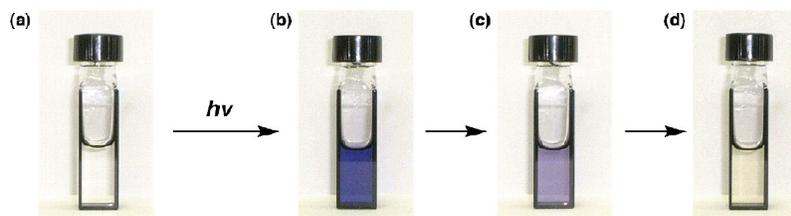


Figure. S3. Coloration of an aqueous solution of **1** \supset (**2**)₄ before and after photo-irradiation at r.t. under argon. (a) before photo-irradiation, (b) after photo-irradiation of **1** \supset (Ad)₄ for 30 min under argon, and (c, d) after the exposure to air.

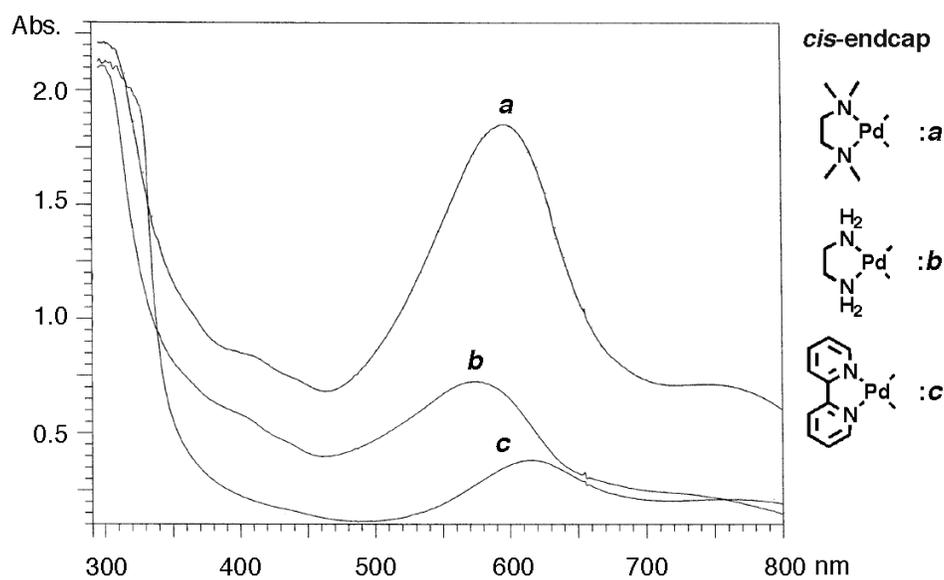


Figure. S4. *Cis*-endcap dependent UV-vis spectra of $\text{cage}\supset(\text{Ad})_4$ after photo-irradiation for 30 min under argon (H_2O , 2.0 mM, r.t.). (a) $\text{M} = (\text{Me}_4\text{en})\text{Pd}(\text{NO}_3)_2$, (b) $\text{M} = (\text{en})\text{Pd}(\text{NO}_3)_2$, and (c) $\text{M} = (\text{Bpy})\text{Pd}(\text{NO}_3)_2$.

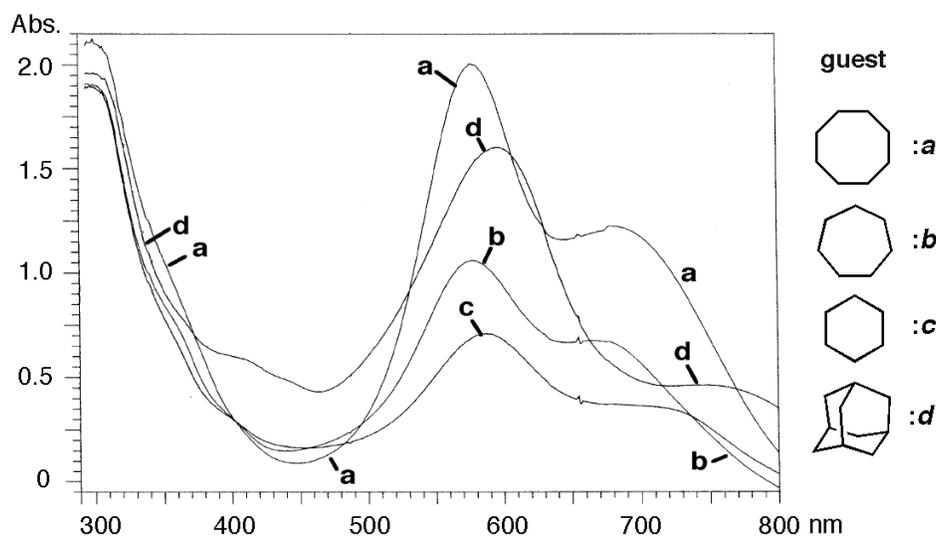


Figure. S5. Guest dependent UV-vis spectra of $1\supset(\text{G})_4$ after photo-irradiation for 30 min under argon (H_2O , 2.0 mM, r.t.). (a) $\text{G} = \text{cyclooctane}$, (b) $\text{G} = \text{cycloheptane}$, (c) $\text{G} = \text{cyclohexane}$, and (d) $\text{G} = \text{adamantane}$.

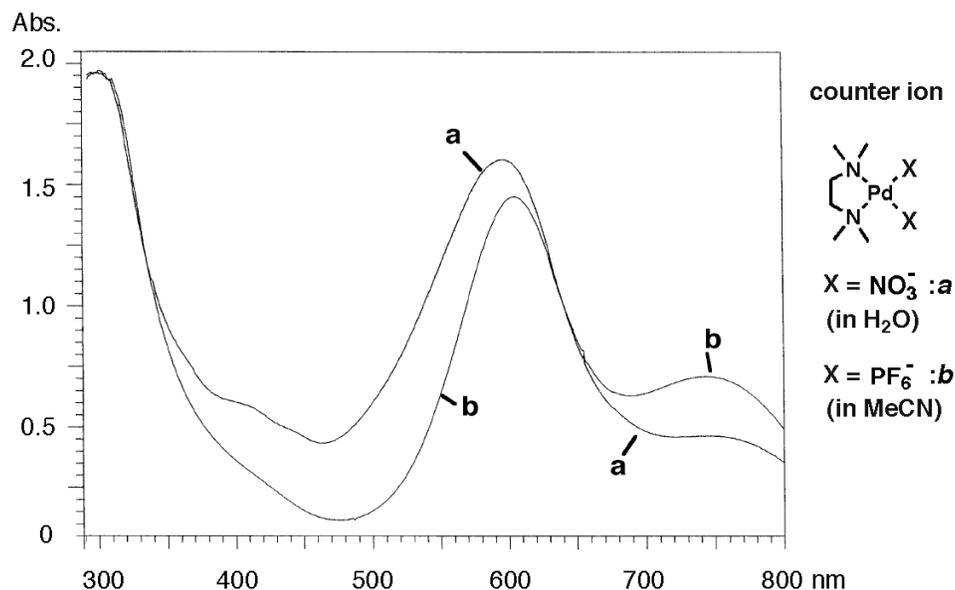


Figure. S6. Counter dependent UV-vis spectra of $1 \supset (\text{Ad})_n$ after photo-irradiation for 30 min under argon (2.0 mM, r.t.). (a) $\text{X} = \text{NO}_3^-$ (in H_2O) and (b) $\text{X} = \text{PF}_6^-$ (in MeCN).

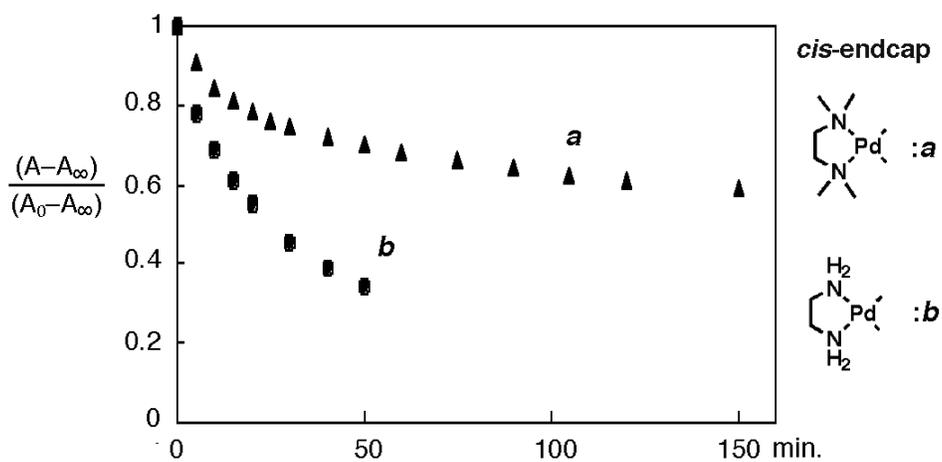


Figure. S7. Plots of the decreasing UV-vis absorbance of radical (blue) species which generated by the photo-irradiation of cage $\supset (\text{Ad})_4$ for 30 min under argon (2.0 mM, r.t.). (a) Cage 1a ($\text{cis-endcap} = (\text{Me}_4\text{en})\text{Pd}(\text{NO}_3)_2$) at $\lambda_{\text{max}} = 593\text{nm}$ and (b) cage 1b ($\text{cis-endcap} = (\text{en})\text{Pd}(\text{NO}_3)_2$) at $\lambda_{\text{max}} = 573\text{nm}$.

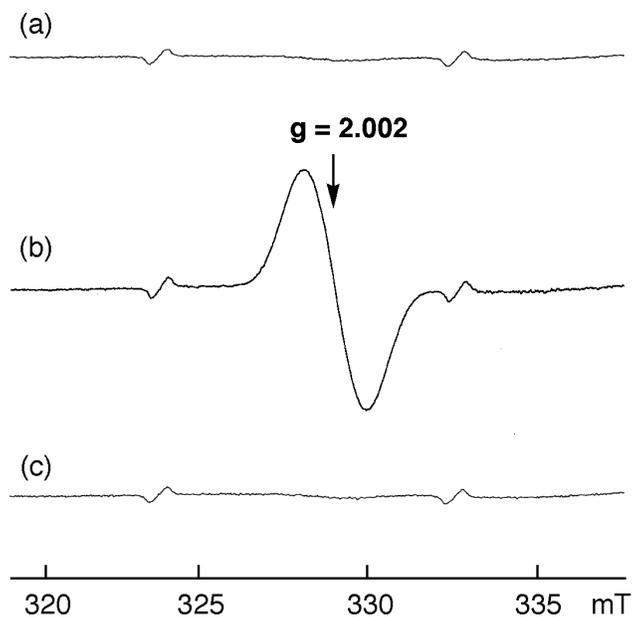


Figure. S8. ESR spectra of 1-(Ad)_4 before and after photo-irradiation (H_2O , 5.0 mM, $-170\text{ }^\circ\text{C}$). (a) before photo-irradiation, (b) after photo-irradiation of 1-(Ad)_4 for 30 min under argon, and (c) after the exposure to air.

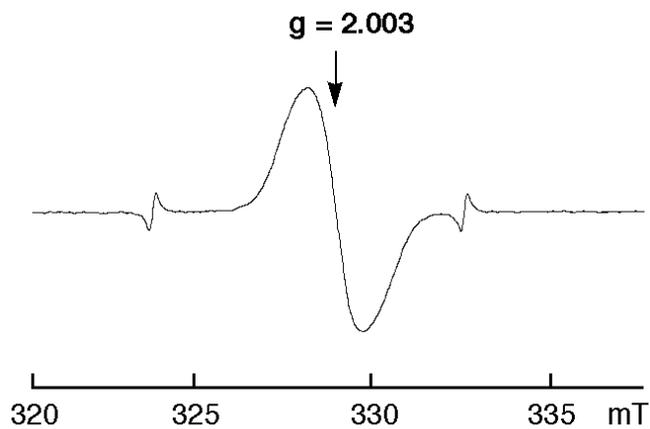


Figure. S9. ESR spectra of $1\text{-(Cycloheptane)}_4$ after photo-irradiation (H_2O , 5.0 mM, $-266\text{ }^\circ\text{C}$) for 30 min under argon.

Table S2. Crystal data and structure refinement for $\mathbf{1}'\supset(2)_4$.

Empirical formula	C172 H160 N48 O36 Pd6	
Formula weight	4108.64	
Temperature	78(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(3)2(1)2	
Unit cell dimensions	a = 29.579(6) Å	a = 90°
	b = 29.579(6) Å	b = 90°
	c = 33.202(9) Å	g = 90°
Volume	29049(11) Å ³	
Z	4	
Density (calculated)	1.123 Mg/m ³	
Absorption coefficient	0.440 mm ⁻¹	
F(000)	9960	
Crystal size	0.25 x 0.25 x 0.20 mm ³	
Theta range for data collection	1.38 to 27.76°	
Index ranges	-38<=h<=38, -38<=k<=38, -43<=l<=42	
Reflections collected	339602	
Independent reflections	33392 [R(int) = 0.1598]	
Completeness to theta = 19.78°	97.8 %	
Absorption correction	Empirical (SADABS)	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	33392 / 1641 / 1486	
Goodness-of-fit on F2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.1109, wR2 = 0.2844	
R indices (all data)	R1 = 0.1775, wR2 = 0.3395	
Largest diff. peak and hole	1.081 and -0.853 eÅ ⁻³	

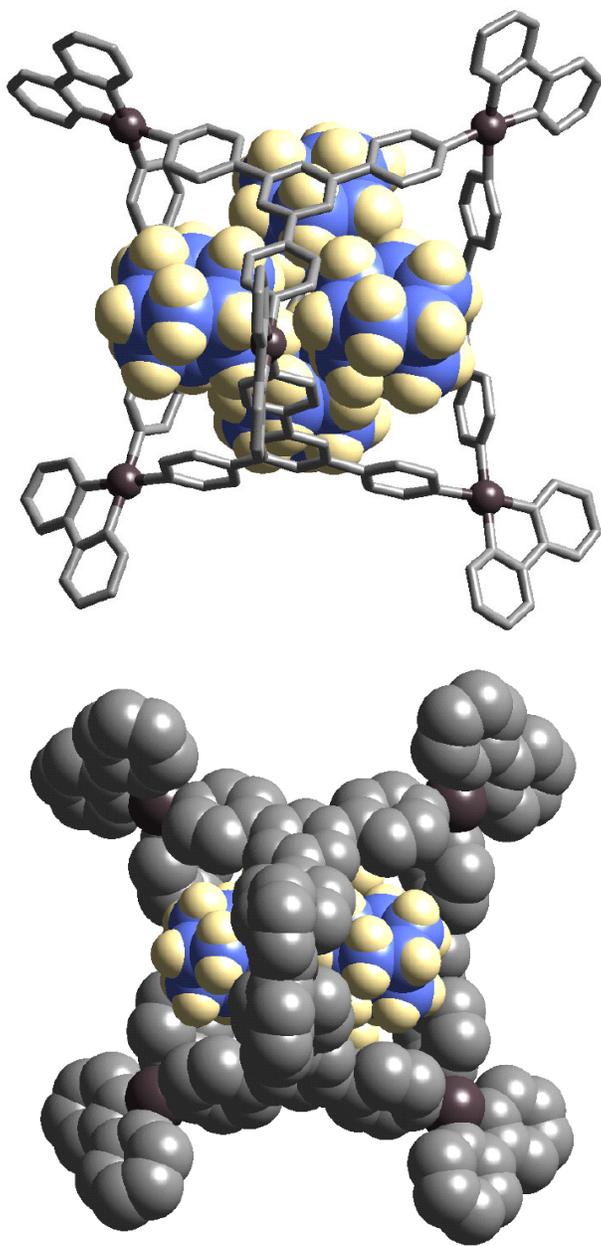


Figure. S10. Crystal structure of $1'-(2)_4$ complex. Cylinder and ball (left), and ball (right) representation.