Electronic Supplementary Information

Halogen anion-induced formation of the heteroleptic binuclear palladium complexes [(PdLHal)$_2$] (Hal = Cl$^-$, Br$^-$, I$^-$) *vs.* homoleptic mononuclear complex [PdL$_2$] of *N*-thiophosphorylated thiourea 6-MeO(O)CC$_6$H$_4$NHC(S)NHP(S)(O*i*Pr)$_2$ (HL). Reversible photoinduced *cis*/*trans* isomerization of [PdL$_2$]

Damir A. Safin,[a] Maria G. Babashkina,*[a] Koen Robeyns[a] and Yann Garcia*[a]

[a] *Institute of Condensed Matter and Nanosciences, MOST - Inorganic Chemistry, Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium. Fax: +32(0) 1047 2330; Tel: +32(0) 1047 2831; E-mail: maria.babashkina@ksu.ru, yann.garcia@uclouvain.be*

Physical measurements: NMR spectra in $CDCl_3$ were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded at 299.948 and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H) and 85% H_3PO_4 (^{31}P{^{1}H}). UV-Vis absorption spectra in 10^{-4} M solutions in CH_2Cl_2 were recorded on a Varian Cary 05E spectrophotometer at 25 °C. Light irradiations were carried out with a standard lamp used for visualizing TLC plates (ROC; intensity at 15 cm from filter: 440 μWcm^{-2} at λ = 254 nm) and with a LOT-ORIEL 200 W high-pressure mercury arc lamp combined with a water cooling setup to avoid infrared light exposure for other wavelengths using appropriate filters. Elemental analyses were performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments.

Synthesis of the Pd^{II} complexes: A suspension of **HL** (0.098 g, 0.25 mmol) in aqueous MeOH (10 mL) was mixed with an aqueous MeOH (10 mL) solution of KOH (0.017 g, 0.3 mmol). An aqueous acetonitrile (10 mL) solution of PdX_2 (X = Cl$^-$, 0.022 g; Br$^-$, 0.033 g; I$^-$, 0.045 g; NO_3^-, 0.029 g; CN$^-$, 0.020 g; CH_3COO^-, 0.028 g; 0.125 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with CH_2Cl_2, washed with water and dried with anhydrous $MgSO_4$. The solvent was then removed in vacuo. Dark or light red solid was isolated and washed with hot *n*-hexane (3 × 10 mL).

[(PdLCl)$_2$]: Yield: 0.122 g (92%). ^{1}H NMR δ: 1.39 (d, $^3J_{H,H}$ = 6.2 Hz, 24H, CH_3, *i*Pr), 3.92 (s, 6H, CH_3, Me), 4.68 (d. sept, $^3J_{POCH}$ = 10.4 Hz, $^3J_{H,H}$ = 6.2 Hz, 4H, OCH), 7.02 (t, $^3J_{H,H}$ = 7.9 Hz, 2H, *m*-H, C_6H_4), 7.44 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, *p*-H, C_6H_4), 7.98 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *o*-H, C_6H_4), 8.63 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-H, C_6H_4), 11.33 (d, $^4J_{PNCNH}$ = 7.6 Hz, 2H, arylNH) ppm. ^{31}P{^{1}H} NMR δ: 51.6 ppm. *Anal*. Calc. for $C_{30}H_{44}Cl_2N_4O_8P_2Pd_2S_4$ (1062.63): C 33.91, H 4.17, N 5.27. Found: C 33.84, H 4.10, N 5.31.

[(PdLBr)$_2$]: Yield: 0.125 g (87%). ^{1}H NMR δ: 1.42 (d, $^3J_{H,H}$ = 6.1 Hz, 24H, CH_3, *i*Pr), 3.90 (s, 6H, CH_3, Me), 4.72 (d. sept, $^3J_{POCH}$ = 10.5 Hz, $^3J_{H,H}$ = 6.1 Hz, 4H, OCH), 7.07 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-H, C_6H_4), 7.42 (t, $^3J_{H,H}$ = 8.0 Hz, 2H, *p*-H, C_6H_4), 8.04 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, *o*-H, C_6H_4), 8.67 (d, $^3J_{H,H}$ = 8.0 Hz, 2H, *m*-H, C_6H_4), 11.39 (d, $^4J_{PNCNH}$ = 7.9 Hz, 2H, arylNH) ppm. ^{31}P{^{1}H} NMR δ: 51.8 ppm. *Anal*. Calc. for $C_{30}H_{44}Br_2N_4O_8P_2Pd_2S_4$ (1151.54): C 31.29, H 3.85, N 4.87. Found: C 31.40, H 3.79, N 4.92.

[(PdLI)$_2$]: Yield: 0.146 g (94%). ^{1}H NMR δ: 1.35 (d, $^3J_{H,H}$ = 6.0 Hz, 24H, CH_3, *i*Pr), 3.95 (s, 6H, CH_3, Me), 4.66 (d. sept, $^3J_{POCH}$ = 10.4 Hz, $^3J_{H,H}$ = 6.1 Hz, 4H, OCH), 7.05 (t, $^3J_{H,H}$ = 7.9 Hz, 2H, *m*-H, C_6H_4), 7.47 (t, $^3J_{H,H}$ = 7.9 Hz,

2H, *p*-H, C_6H_4), 7.93 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, *o*-H, C_6H_4), 8.58 (d, $^3J_{H,H}$ = 7.9 Hz, 2H, *m*-H, C_6H_4), 11.47 (d, $^4J_{PNCNH}$ = 7.8 Hz, 2H, arylNH) ppm. $^{31}P\{^1H\}$ NMR δ: 51.5 ppm. *Anal*. Calc. for $C_{30}H_{44}I_2N_4O_8P_2Pd_2S_4$ (1245.54): C 28.93, H 3.56, N 4.50. Found: C 28.82, H 3.59, N 4.47.

[PdL$_2$]: Yield: 0.106 g (96%) obtained from $Pd(NO_3)_2$; 0.094 g (85%) obtained from $Pd(CN)_2$; 0.101 g (91%) obtained from $Pd(CH_3COO)_2$. ^1H NMR δ: 1.39 (d, $^3J_{H,H}$ = 6.1 Hz, CH_3, *i*Pr), 1.40 (d, $^3J_{H,H}$ = 6.1 Hz, CH_3, *i*Pr), 1.43 (d, $^3J_{H,H}$ = 6.2 Hz, CH_3, *i*Pr), 1.44 (d, $^3J_{H,H}$ = 6.2 Hz, CH_3, *i*Pr), 3.93 (s, CH_3, Me), 3.94 (s, CH_3, Me), 4.76 (d. sept, $^3J_{POCH}$ = 10.1 Hz, $^3J_{H,H}$ = 6.1 Hz, OCH), 4.92 (d. sept, $^3J_{POCH}$ = 10.4 Hz, $^3J_{H,H}$ = 6.2 Hz, OCH), 7.06 (br. t, $^3J_{H,H}$ = 7.9 Hz, *m*-H, C_6H_4), 7.45 (br. t, $^3J_{H,H}$ = 7.9 Hz, *p*-H, C_6H_4), 7.99 (d, $^3J_{H,H}$ = 7.9 Hz, *o*-H, C_6H_4), 8.46–8.67 (m, *m*-H, C_6H_4), 11.39 (d, $^4J_{PNCNH}$ = 6.6 Hz, arylNH), 11.44 (d, $^4J_{PNCNH}$ = 6.6 Hz, arylNH) ppm. $^{31}P\{^1H\}$ NMR δ: 50.0 (1P), 52.0 (5P) ppm. *Anal*. Calc. for $C_{30}H_{44}N_4O_8P_2PdS_4$ (885.31): C 40.70, H 5.01, N 6.33. Found: C 40.82, H 4.98, N 6.37.

X-Ray crystallography: The X-ray data were collected on a MAR345 image plate, with Mo-K_α radiation (Zr filter) generated by a Rigaku UltraX 18 rotationg anode. The reflections of the images were indexed and integrated using the CrysalisPro package (Agilent Technologies).[1] Data were scaled and corrected for absorption using the integrated scale3 abspack procedure. The structures were solved by direct methods using the SHELXS-97 program[2] and refined first isotropically and then anisotropically using SHELXL-97.[2] Hydrogen atoms were placed at calculated positions and refined in riding mode with respect to the parent atoms. The crystal packing of **[(PdLCl)$_2$]** contains one void (96 Å^3, around an inversion center) which has been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[3] A total of eight electrons were located in the void, corresponding to one H_2O molecule. Formula, density include the diffuse contribution of the H_2O molecule. Figures were generated using the program Mercury.[4]

Crystal data for [(PdLCl)$_2$]: $C_{30}H_{44}Cl_2N_4O_8P_2Pd_2S_4$, H_2O; M_r = 1080.59 g mol^{-1}, triclinic, space group $P\ \bar{1}$, a = 8.6119(9), b = 11.1471(14), c = 13.3906(9) Å, α = 106.140(9), β = 99.678(7), γ = 108.160(10)°, V = 1126.7(2) Å^3, Z = 1, ρ = 1.566 g cm^{-3}, μ(Mo-Kα) = 1.222 mm^{-1}, reflections: 6570 collected, 2535 unique, R_{int} = 0.046, R_1(all) = 0.0654, wR_2(all) = 0.1819.

Crystal data for [PdL$_2$]·1,4-dioxane: $C_{30}H_{44}N_4O_8P_2PdS_4$, $C_4H_8O_2$, M_r = 973.38 g mol^{-1}, triclinic, space group $P\ \bar{1}$, a = 9.3910(5), b = 9.6617(10), c = 13.2526(14) Å, α = 111.262(10), β = 104.326(7), γ = 92.377(7)°, V = 1074.23(19) Å^3, Z = 1, ρ = 1.505 g cm^{-3}, μ(Mo-Kα) = 0.757 mm^{-1}, reflections: 8795 collected, 3669 unique, R_{int} = 0.037, R_1(all) = 0.0304, wR_2(all) = 0.0824.

CCDC 852935 (**[(PdLCl)$_2$]**) and 852936 (**[PdL$_2$]·1,4-dioxane**) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

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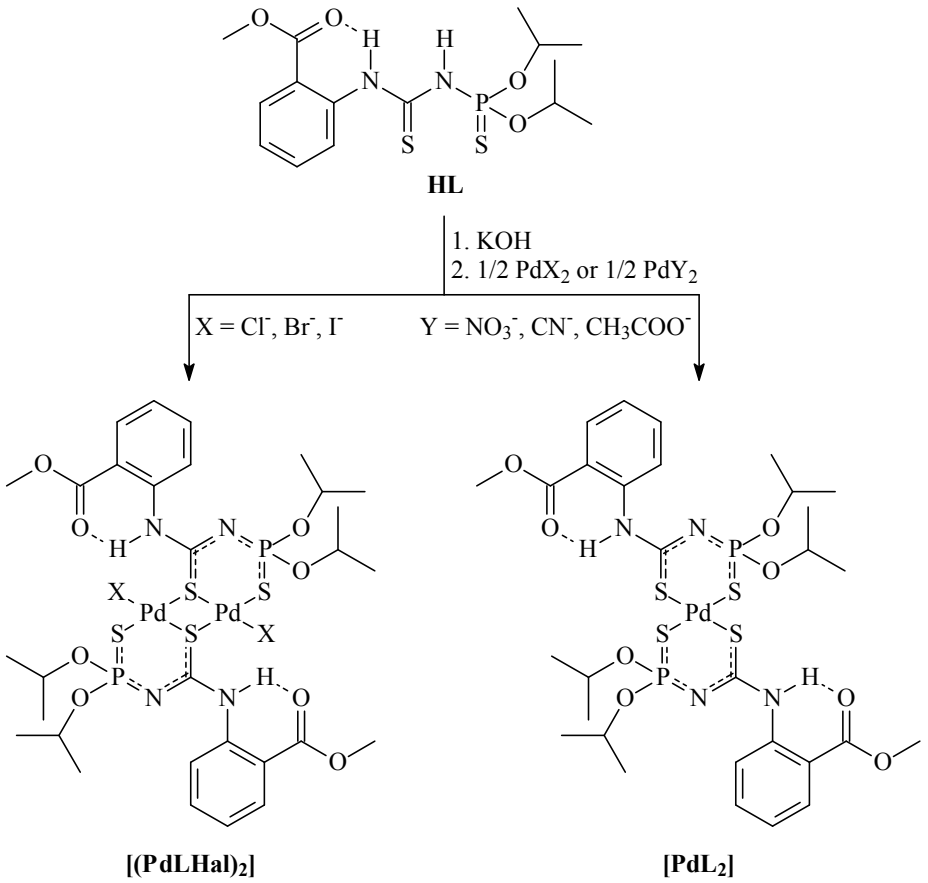
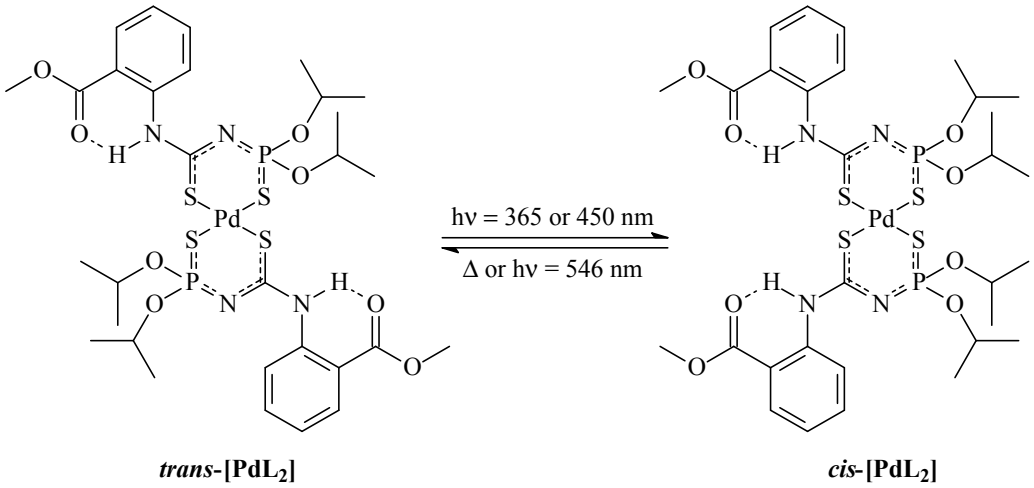


Scheme S1



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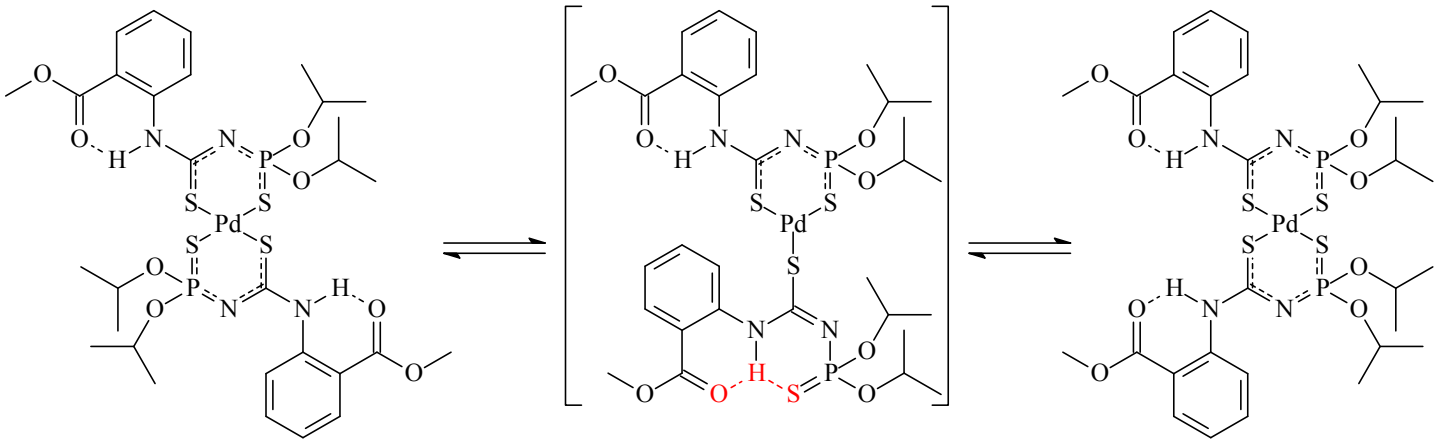

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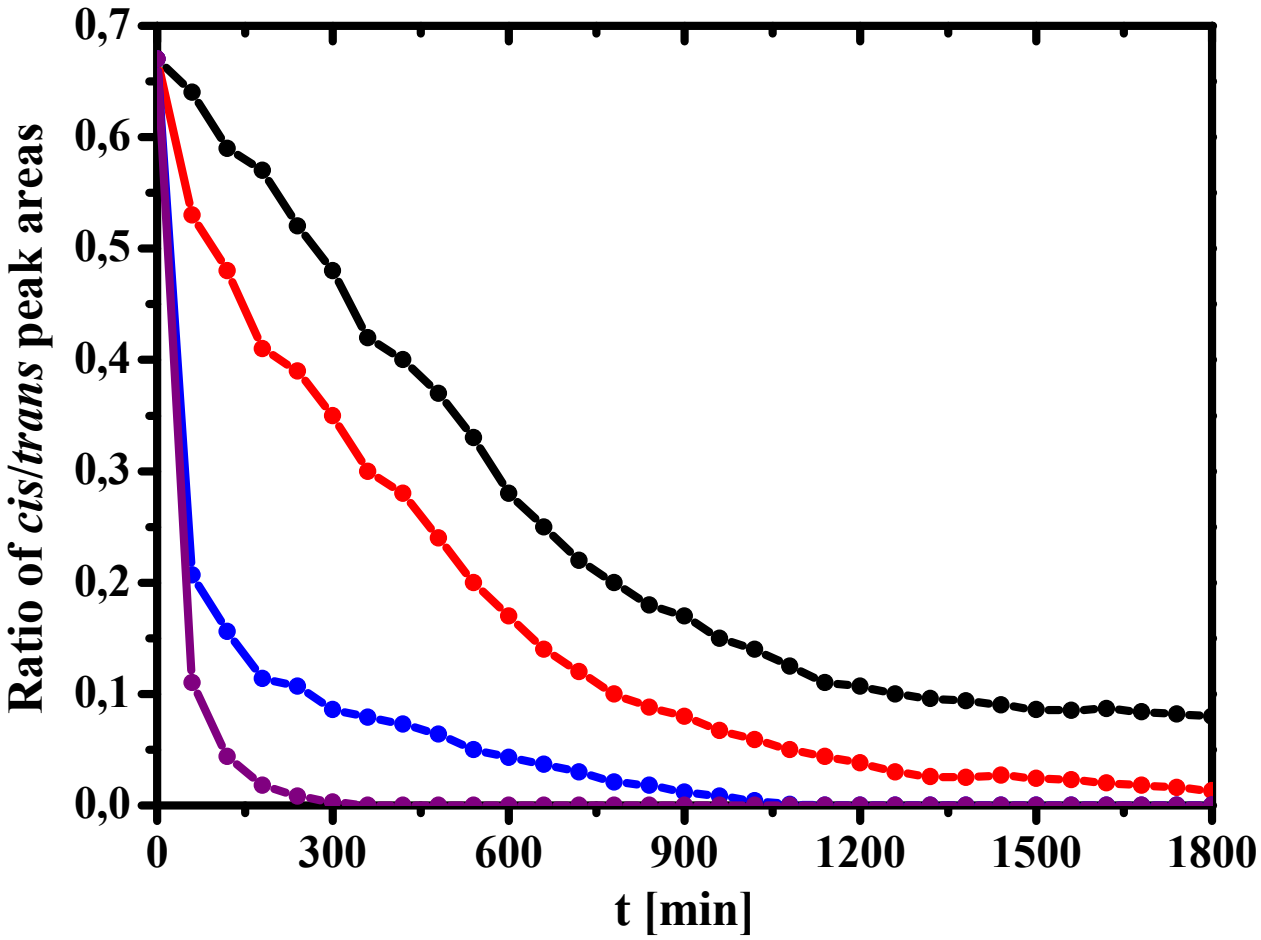

Fig. S1 The $^{31}P\{^{1}H\}$ NMR monitored ratio of *cis*/*trans* peak areas for **[PdL$_2$]** in $CDCl_3$ (0.1 M) kept in darkness after irradiation at λ = 365 nm at –25°C (black), 0°C (red), 25°C (blue) and 50°C (purple).

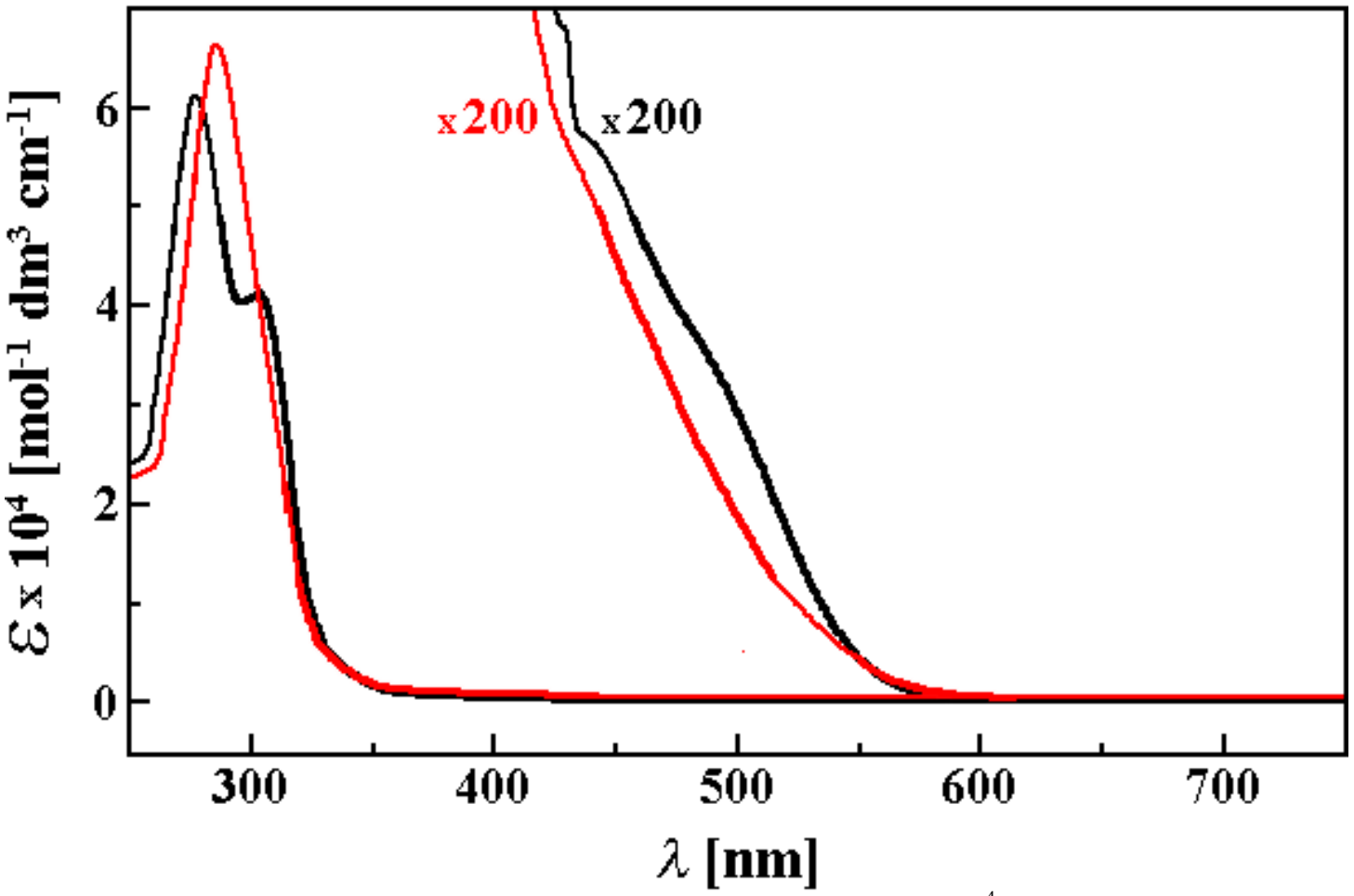

Fig. S2 The UV-vis spectra of the freshly prepared sample of **[PdL$_2$]** in CH_2Cl_2 (10^{-4} M) recorded in darkness (red) and after irradiation at λ = 365 nm (black).

Table S1. Selected bond lengths (Å) and angles (°) for **[(PdLCl)$_2$]**

Bond lengths					
Pd(1)–Cl(2)	2.362(3)	C(14)–N(15)	1.319(15)	P(4)–O(5)	1.561(9)
Pd(1)–S(3)	2.327(3)	C(14)–S(21)	1.809(12)	P(4)–O(9)	1.563(8)
Pd(1)–S(21)	2.297(3)	P(4)–N(13)	1.627(10)	C(22)–O(23)	1.202(16)
Pd(1)–S(21)a	2.312(3)	P(4)–S(3)	2.003(5)	C(22)–O(24)	1.322(16)
C(14)–N(13)	1.295(14)				
Bond angles					
Pd(1)–S(21)–Pd(1)a	98.30(12)	S(3)–Pd(1)–S(21)a	170.43(12)	O(5)–P(4)–N(13)	105.7(5)
Pd(1)–S(3)–P(4)	104.40(14)	S(21)–Pd(1)–S(21)a	81.70(11)	O(9)–P(4)–N(13)	107.7(5)
Pd(1)–S(21)–C(14)	103.5(4)	C(14)–S(21)–Pd(1)a	114.4(4)	O(5)–P(4)–O(9)	102.9(4)
Cl(2)–Pd(1)–S(3)	87.47(11)	N(13)–C(14)–N(15)	123.8(10)	S(3)–P(4)–N(13)	115.6(4)
Cl(2)–Pd(1)–S(21)	174.23(10)	P(4)–N(13)–C(14)	125.4(8)	S(3)–P(4)–O(5)	115.5(3)
Cl(2)–Pd(1)–S(21)a	93.01(11)	S(21)–C(14)–N(13)	120.9(9)	S(3)–P(4)–O(9)	108.5(3)
S(3)–Pd(1)–S(21)	98.13(11)	S(21)–C(14)–N(15)	115.3(8)		

Table S2. Selected bond lengths (Å) and angles (°) for **[PdL$_2$]·1,4-dioxane**

Bond lengths					
Pd(1)–S(2)	2.3256(8)	C(5)–S(6)	1.747(3)	P(3)–O(11)	1.562(2)
Pd(1)–S(6)	2.3059(8)	P(3)–N(4)	1.604(2)	C(22)–O(23)	1.215(4)
C(5)–N(4)	1.310(4)	P(3)–S(2)	2.0029(11)	C(22)–O(24)	1.335(3)
C(5)–N(15)	1.367(3)	P(3)–O(7)	1.576(2)		
Bond angles					
Pd(1)–S(2)–P(3)	101.45(4)	N(4)–C(5)–N(15)	120.1(3)	O(11)–P(3)–N(4)	105.37(13)
Pd(1)–S(6)–C(5)	116.79(9)	P(3)–N(4)–C(5)	127.5(2)	O(7)–P(3)–O(11)	104.07(11)
S(2)–Pd(1)–S(6)	97.80(3)	S(6)–C(5)–N(4)	130.7(2)	S(2)–P(3)–N(4)	118.24(12)
S(2)–Pd(1)–S(2)a	180.00	S(6)–C(5)–N(15)	109.2(2)	S(2)–P(3)–O(7)	106.76(9)
S(2)–Pd(1)–S(6)a	82.20(3)	O(7)–P(3)–N(4)	107.42(13)	S(2)–P(3)–O(11)	113.94(9)

Table S3. Hydrogen bond lengths (Å) and angles (°) for **[(PdLCl)$_2$]** and **[PdL$_2$]·1,4-dioxane**

Complex	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
[(PdLCl)$_2$]	N(15)–H(15)···O(23)	0.86	2.14	2.671(13)	120
[PdL$_2$]·1,4-dioxane	N(15)–H(15)···O(23)	0.88	1.96	2.638(3)	133