Supplementary Material (ESI) for Chemical Communications

Dr. Jorge A. R. Navarro
Profesor Titular de Universidad
Departamento Quimica Inorganica
Universidad de Granada
Av. Fuentenueva S/N
Granada, E-18071
Spain
Tel. +34-958248093
Fax: +34-958248526
E-mail: jarn@ugr.es

Supporting Information

for

Electrochemically and Photochemically Active Palladium(II) Heterotopic Metallacalix[3]arenes

Miguel A. Galindo, Andrew Houlton*, William Clegg, Ross W. Harrington, José Dobado, Francisco J. Santoyo-Gonzalez, M. Angustias Romero* and Jorge A. R. Navarro*

Experimental

Methods

Electrochemistry: Cyclic voltammograms were carried out using a CH instrument Model 700B Series Electrochemical Analyzer/Workstation and a three-electrode configuration; Au or Pt working electrode, Pt counter electrode, Ag/AgCl reference. **2b**: A 1.2 mM solution of **2b** in acetonitrile, 120 mM of $LiClO_4$ at room temperature. **3b**: A 1:1 water-methanol mixture containing 1 mM **3b**, 100 mM $LiClO_4$ at room temperature. Titration experiment: a 1:1 water-methanol mixture containing 4 mM **3b,** 100 mM $LiClO_4$ was titrated with Ur. Kass was determinated by non-linear regression. The uncertainly in Kass was estimated by a boot strap method. [Ref: W. H. Press, S. A. Teukolsky, W. T. Vetterling and B. P. Flannery, Numerical Recipes in Fortran, Cambridge University Press, Cambridge, 2nd edn., 1992]

Electronic structure calculations: all calculations were performed using Spartan software (Spartan SGI version 5.1.1 Wavefunction, 18401 Von Karman, Suite 370, Irvine, CA 92612, USA) running on a SGI workstation. Geometry optimization were carried out with a DFT method at the B3LYP/3-21G(*) level.

Synthesis

5-Ethynylferrocene-2-hydroxypyrimidine (**2b**): 5-iodo-2-hydroxypyrimidine[Error! Bookmark not defined.] (0.222 g, 1 mmol) was dissolved in dry and deoxygenated piperidine. Ethynylferrocene (0.218 g, 1 mmol,), CuI (0.028 g, 0.15 mmol) and bis(triphenylphosphine)dichloropalladium(II) (0.07 g, 0.1 mmol) were added sequentially under a N_2 atmosphere. The reaction mixture was stirred at 60 ºC for 5h. Disodium EDTA (5% v/w) (5 mL) was added to the resulting suspension before evaporation to dryness. The crude product was redissolved in chloroform (100 mL) and washed twice with disodium EDTA (5% v/w) and once with water before being dried over sodium sulfate. After filtration and concentration by rotary evaporation the reaction mixture was loaded onto a silica gel column packed in chloroform and eluted by using chloroform-methanol (95:5). Fractions containing the product were combined and solvent removed to yield the title compound as a dark orange powder (0.130 g, 44%). ^{1}H NMR (400 MHz, MeOD-d_4, 25 °C): δ(ppm) = 4.14 (s, 5H; Fc), 4.20 (m, 2H; Fc), 4.38 (m, 2H; Fc), 8.30 (s, 2H; $H_{4,4'}$ efpymo). ESI-MS: m/z (positive mode) 304.03. (calcd for 5-ethynylferrocene-2-hydroxypyrimidine, 304.03).

†5-{5'-(Dimethylamino)-1-naphthalenesulfonamide-N-(2'-propynyl-1'-yl)}-2-hydroxypyrimidine (**2c**): 5-iodo-2-hydroxypyrimidine[Error! Bookmark not defined.] (2 mmol, 0.446 g) and 5-(dimethylamino)-N-(2-propynyl)-1-naphthalenesulfonamide[Error! Bookmark not defined.] (0.576

g, 2 mmol were reacted in a similar way to **2b**. The product was obtained as a dark orange powder (0.270 g, 35%). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ(ppm) = 2..83 (s, 6H; dansyl), 3.98 (d, 2H; CH2 propargyl), 5.23 (broad, 1H; NH propargyl) 7.16 (d, 1H; dansyl), 7.56 (d, 2H; dansyl), 7.71 (s, 2H; pymo), 8.23 (d, 1H; dansyl), 8.31 (d, 1H; dansyl), 8.50 (d, 1H; dansyl), 8.64 (broad, 1H; pymo). ESI-MS: m/z (positive mode) 405.09 $[M+Na]^+$. Electronic spectra: absorption 413 nm; emission: 547 nm.

† Preparation of $[Pd_3(en)_3(4,7\text{-phen})_2(5\text{-ethynylferrocenepyrimidin-2-olate})](NO_3)_5$ (**3b**) and $[Pd_3(en)_3(4,7\text{-phen})_2(5\text{-}\{5'\text{-(dimethylamino)-1-naphthalenesulfonamide-N-(2'-propynyl-1'-yl)}\}\text{pyrimidin-2-olate})](NO_3)_5$ (**3c**): 1 mL of a MeOD solution of 5-ethynylferrocene-2-hydroxypyrimidine (0.005 mmol, 1.5 mg) was mixed with a D_2O solution of $[Pd_3(en)_3(4,7\text{-phen})_3](NO_3)_6$ (0.005 mmol, 7.1 mg in 1 mL). The solution was heated for 4h at 50 ºC. **3b**: ^{1}H NMR (400 MHz, MeOD-d_4 / D_2O, 25 ºC): δ(ppm) = 2.93-3.07 (m, 24H; en), 4.00 (s, 5H; Fc), 4.08 (m, 2H; Fc), 4.18 (m, 2H; Fc), 7.87 (dd, $J_{1,2}$ = 3.2 Hz, $J_{2,3}$ = 5 Hz; 4H; $H_{2,2'}$phen) 8.13 (s, 2H; $H_{4,4'}$ efpymo), 9.27 (d, 2H; H_1 phen), 9.28 (d, 2H; $H_{1'}$ phen), 9.53 (d, 2H; H_3 phen), 9.78 (d, 2H; $H_{3'}$ phen), 10.47 (d, $J_{5,5'}$ = 9.7 Hz, 2H; H_5 phen), 10.59 (d, 2H; $H_{5'}$ phen). ESI-MS: m/z 1472.013 (calcd. for **3b**-H: 1472.011).

3c: δ(ppm)= 2.5 (s, dansyl), 2.75-3.01 (m, en), 6.94 (s, dansyl), 7.01 (m, dansyl), 7.12 (s, dansyl), 7.59 (s, dansyl), 7.55 (m, $H_{2,2'}$_phen), 8.27 (s, dansyl), 8.53 (s, dansyl), 8,91 (m, H1,1'_phen), 9.41 (d, $J_{2,3'}$ = 5.1 Hz, H_3_phen), 9.48 (d, $H_{3'}$_phen), 10.17 (d, $J_{5,5'}$ = 9.3 Hz; H_5_phen), 10.24 (d, $H_{5'}$_phen). Electronic spectra: absorption 394 nm; emission: 535 nm.

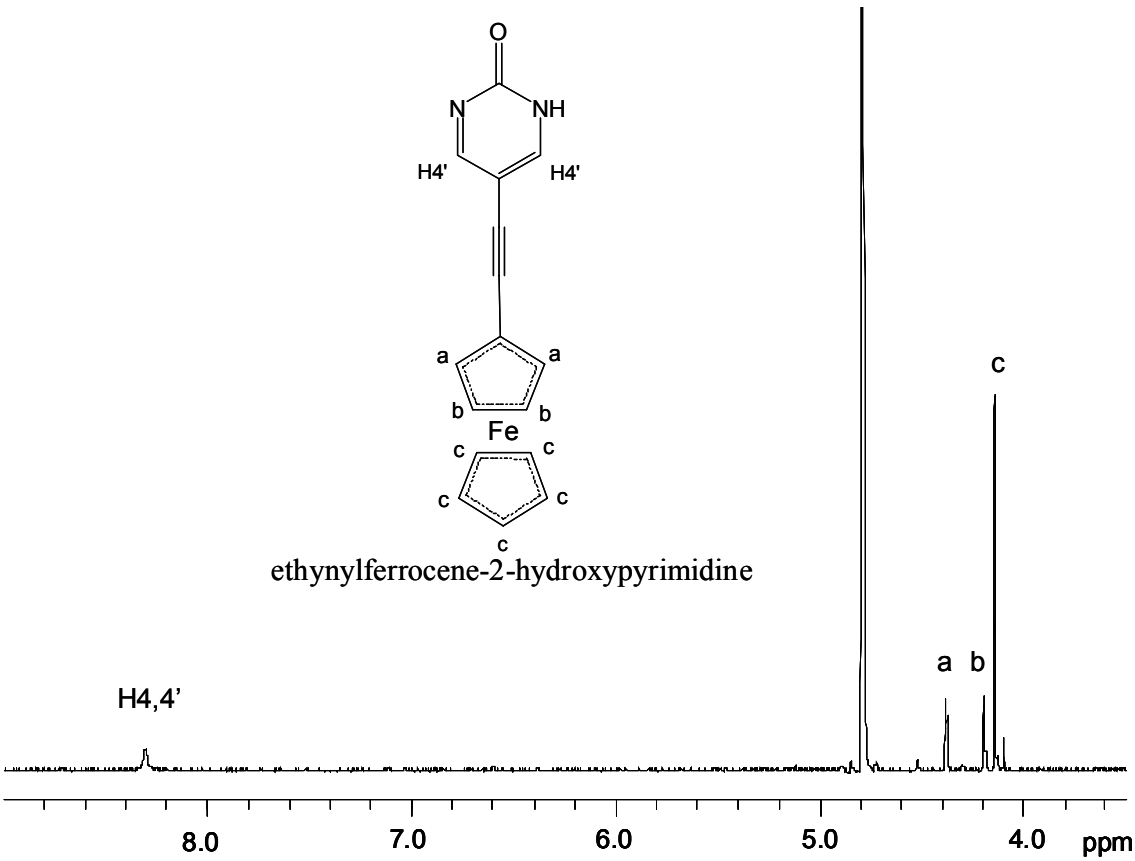

Figure S1.- ^{1}H NMR spectrum (in MeOD-d_4) of 5-ethynylferrocene-2-hydroxypyrimidine (**2b**).

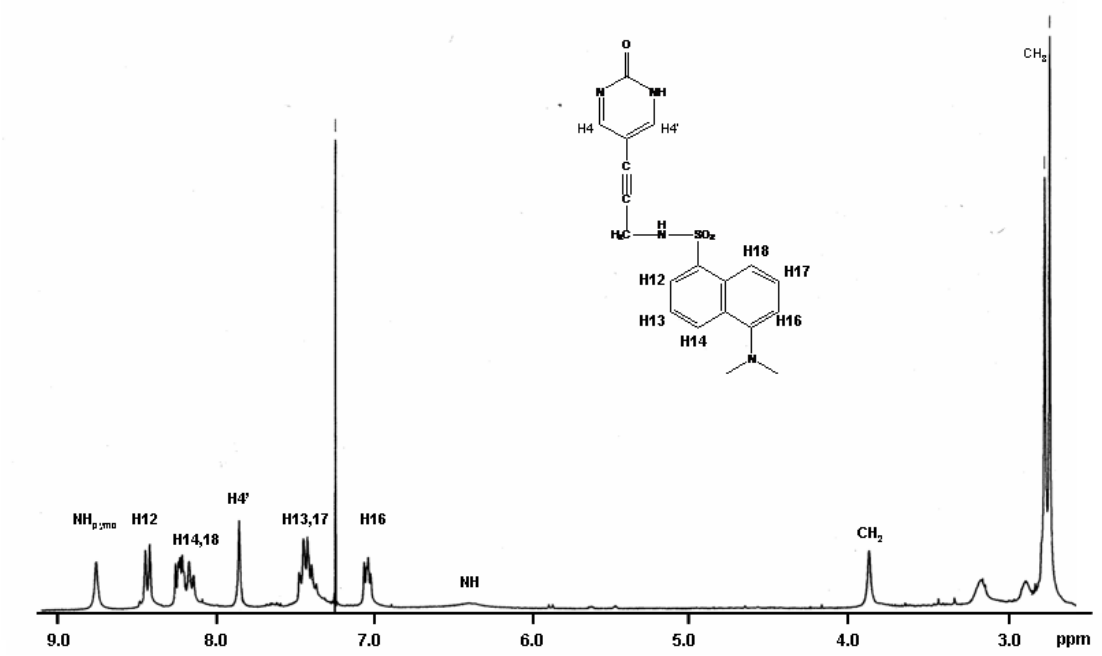

Figure S2.- ^{1}H NMR spectrum (in $CDCl_3$) of 5-{5'-(dimethylamino)-N(2'-propynyl-1'-yl)-1-naphthalenesulfonamide}-2-hydroxypyrimidine (**2c**).

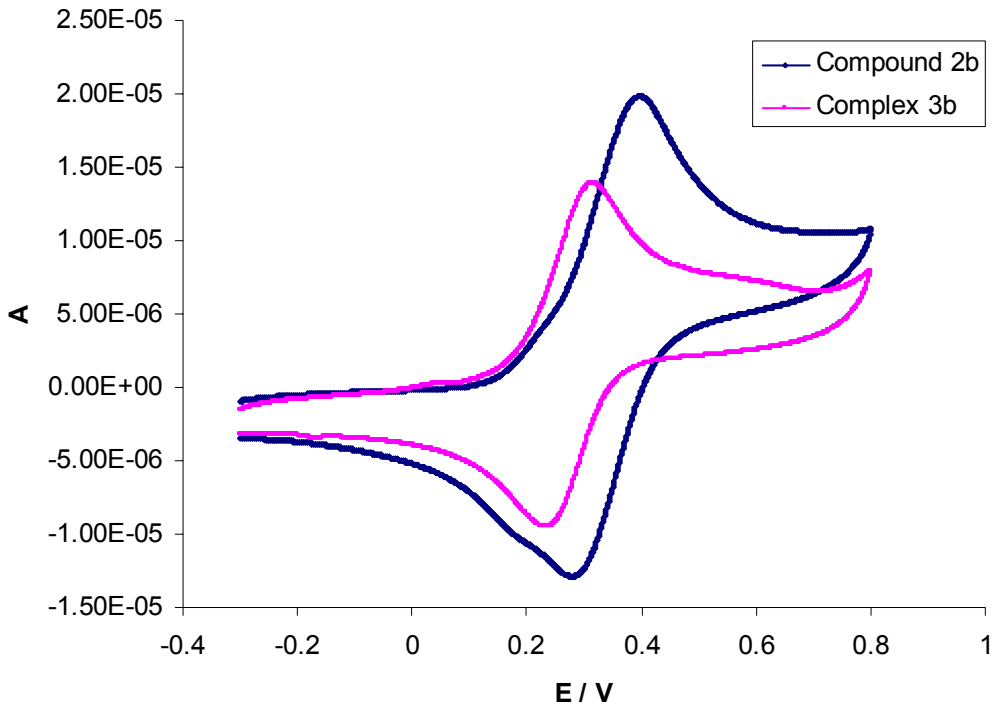

Figure S3.- Cyclic voltammogram of (a) free **2b** and (b) complex **3b**. Conditions: 4mM sample, 100 mM $LiClO_4$ in water/methanol solution, room temperature, working electrode of Pt.

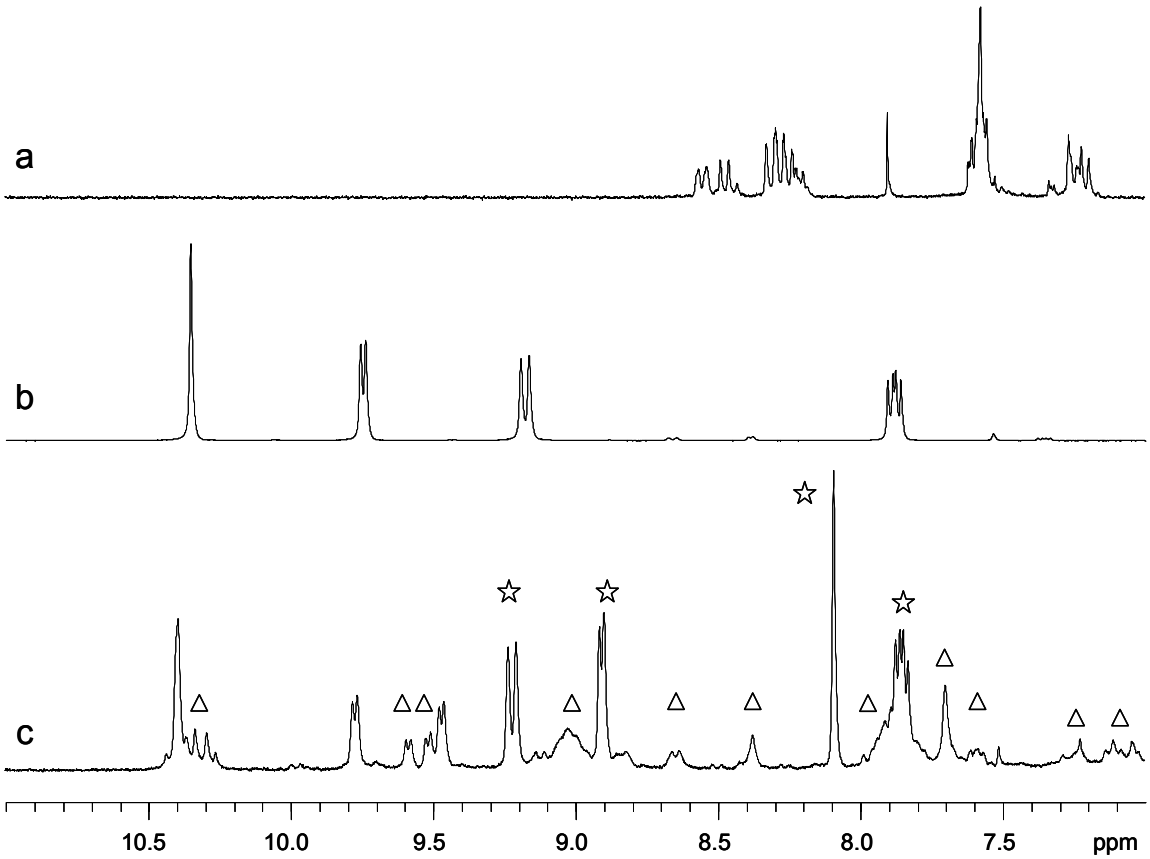

Figure S4. Aromatic region of ^{1}H NMR (MeOD:D_2O, 293 K, 400 MHz). a= 5-ethynyldansylpropargylamine-2-hydroxypyrimidine (**2c**); b= homotopic $[Pd_3(en)_3(4,7\text{-phen})_3]^{6+}$ (1); c= 1:1 reaction mixture of **1** and **2c** after 4 h at 60 ºC. $[Pd_3(en)_3(4,7\text{-phen})_2(5\text{-}\{5'\text{-(dimethylamino)-1-naphthalenesulfonamide-N-(2'-propynyl-1'-yl)}\}\text{pyrimidin-2-olate})](NO_3)_5$ (**3c**) (triangles), free phenanthroline (stars).

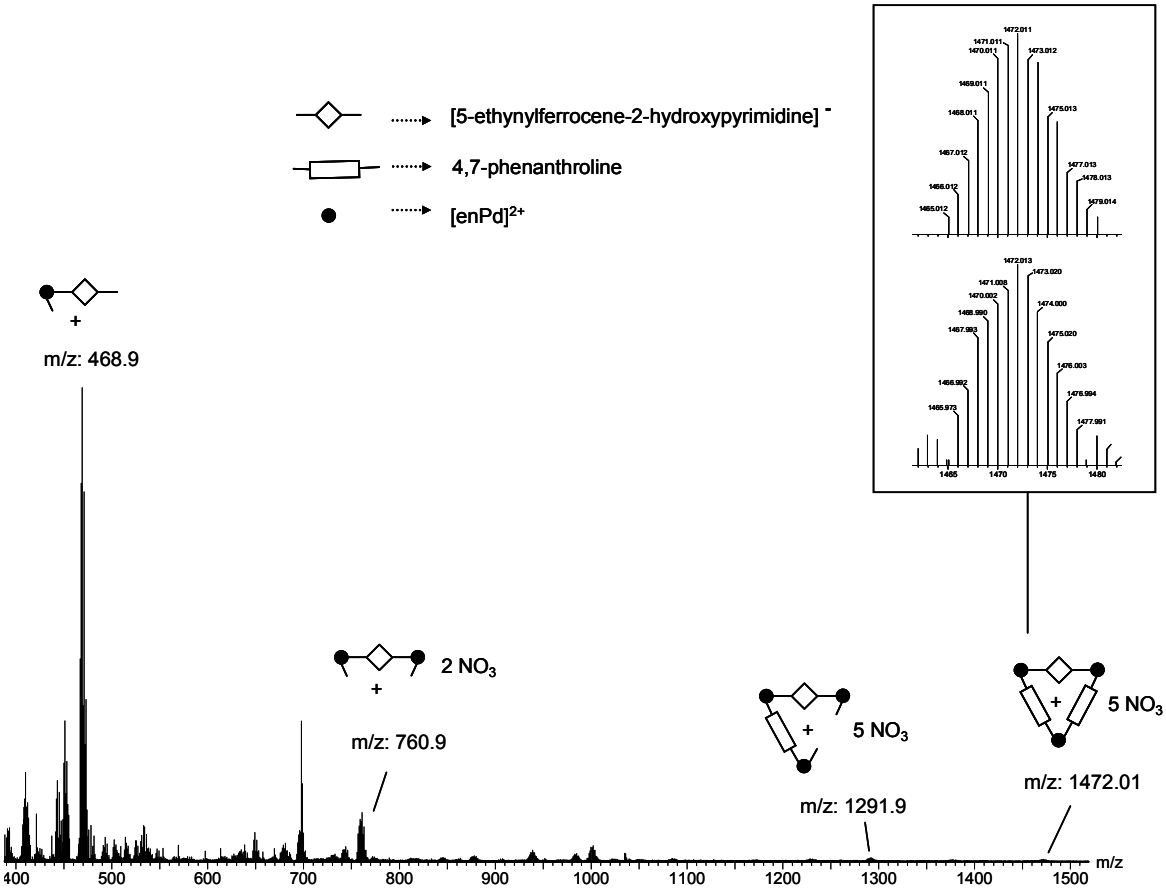

Figure S5. ESI-MS of $[Pd_3(en)_3(4,7\text{-phen})_2(5\text{-ethynylferrocenepyrimidin-2-olate})](NO_3)_5$ (**3b**) in a methanol solution. The insert shows the measured (bottom) and simulated (top) isotopic pattern at m/z 1472.01

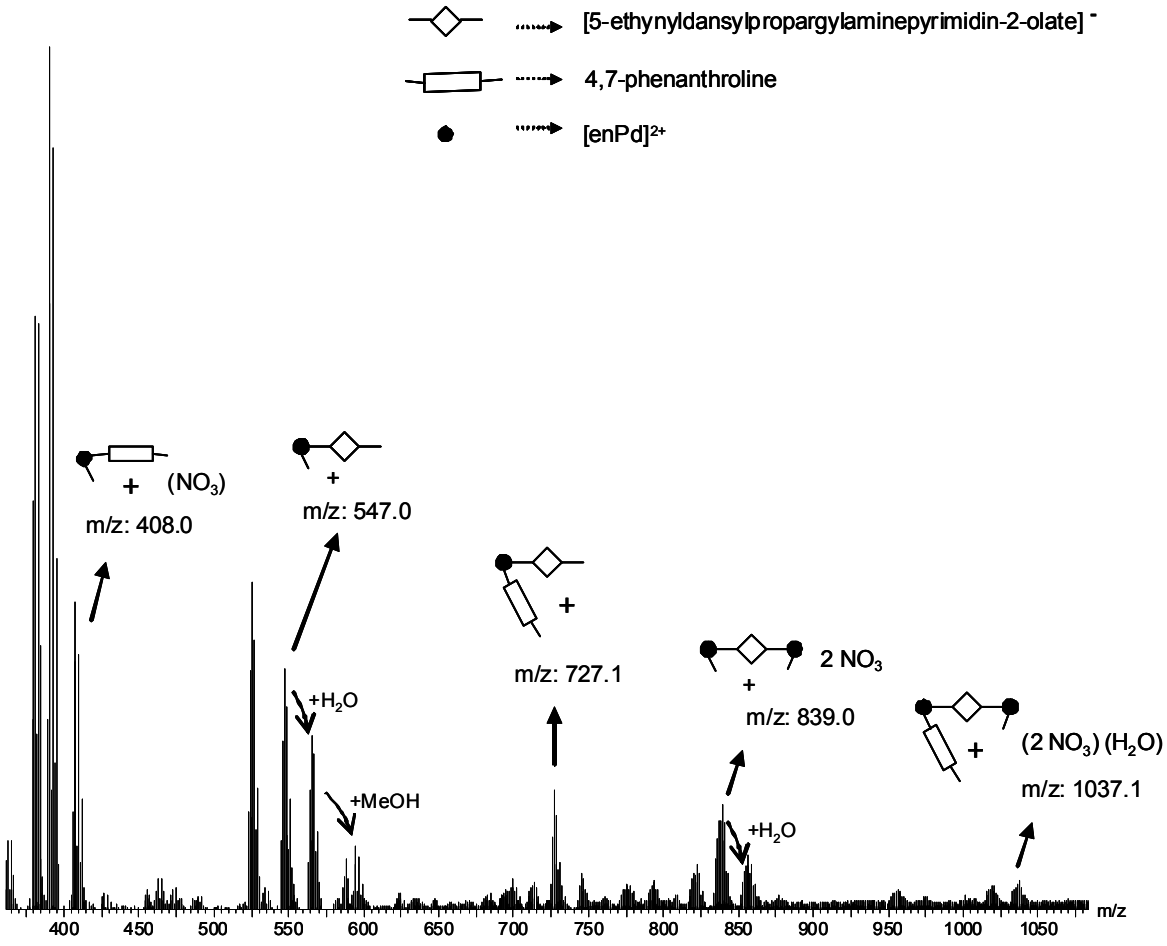

Figure S6. ESI-MS of $[Pd_3(en)_3(4,7\text{-phen})_2(5\text{-}\{5'\text{-}(dimethylamino)\text{-}1\text{-}naphthalenesulfonamide-N-}(2'\text{-propynyl-}1'\text{-yl})\}pyrimidin\text{-}2\text{-}olate)](NO_3)_5$ (**3c**) in methanol solution.

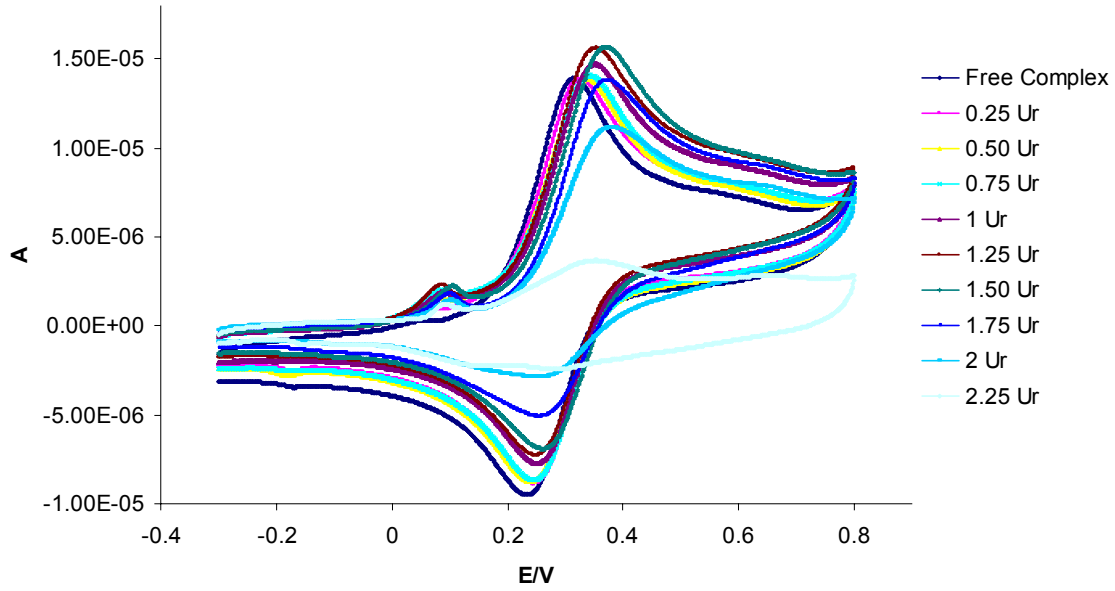

Figure S7.- Cyclic votammograms for the titration of $[Pd_3(en)_3(4,7\text{-phen})_2(5\text{-ethynylferrocenepyrimidin-2-olate})](NO_3)_5$ (**3b**) (4mM) with Ur.

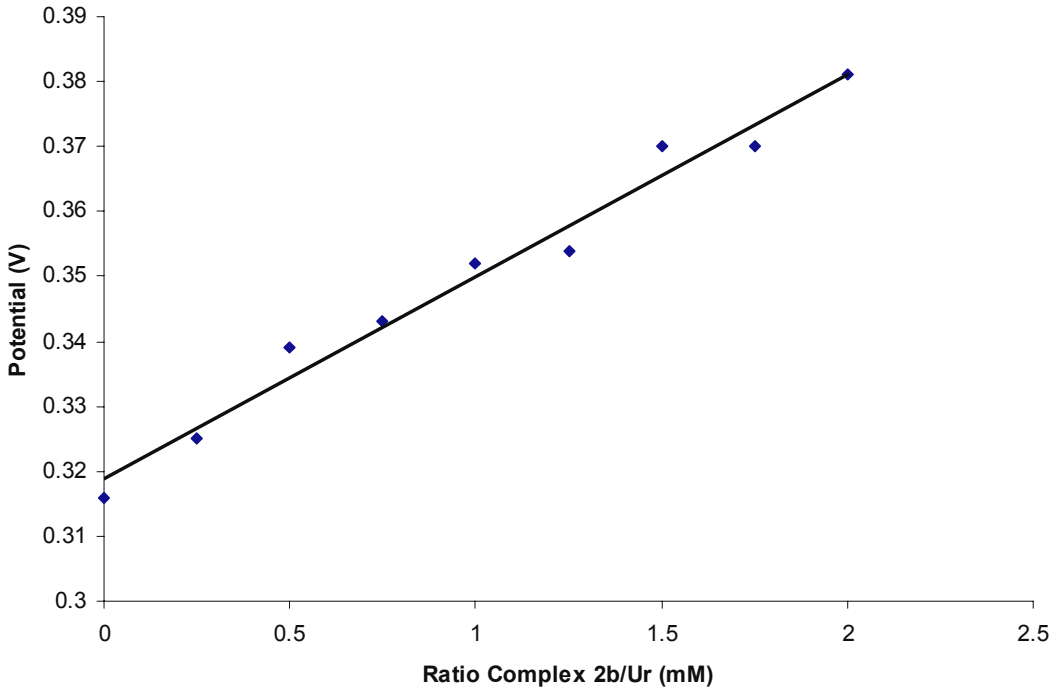

Figure S8.- Plot Potential vs Ratio **3b**/Ur

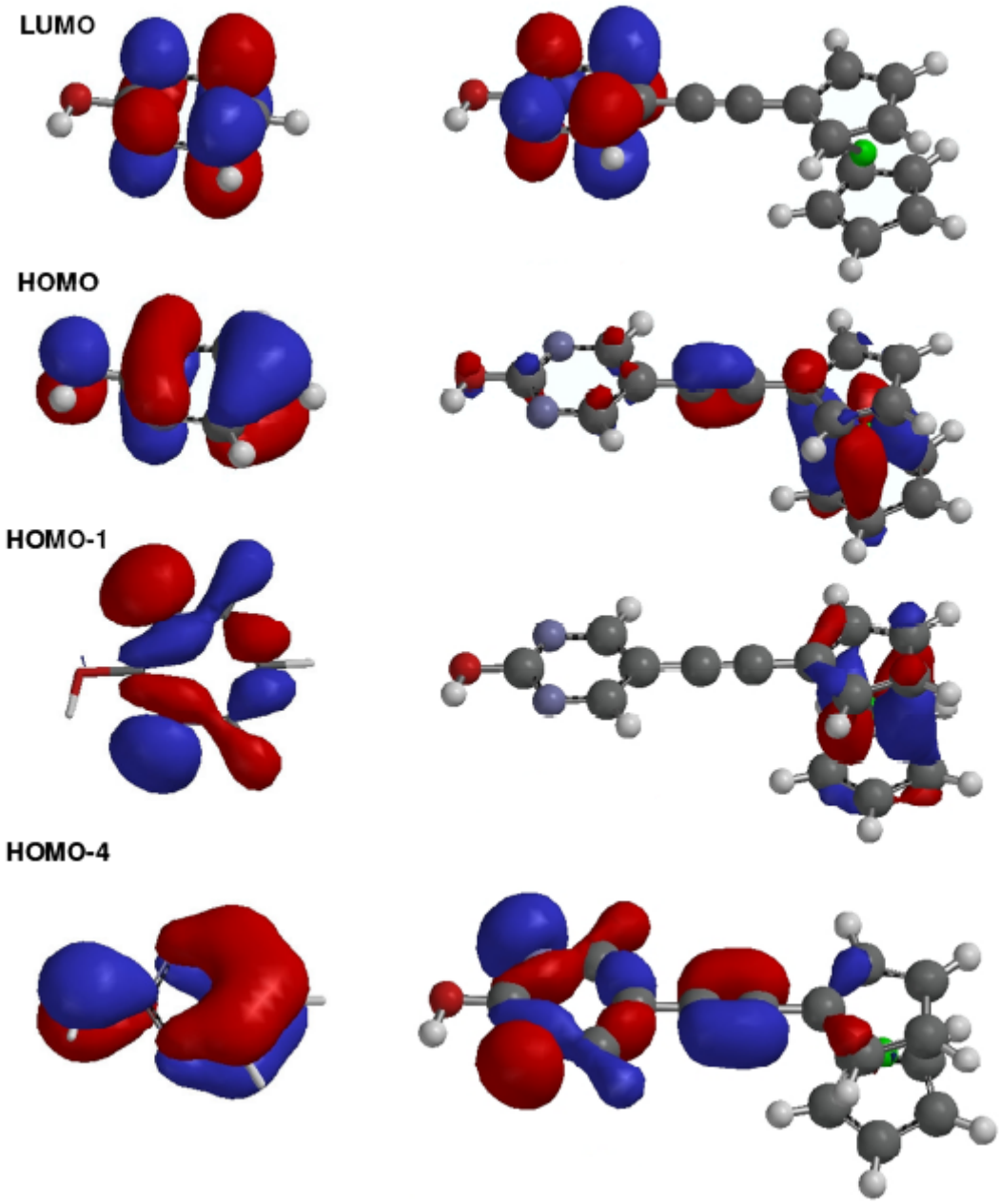

Figure S9. Selected molecular orbitals for the 2-hydroxypyrimidine (**2a**) and 5-ethynylferrocene-2-hydroxypyrimidine derivative (**2b**)

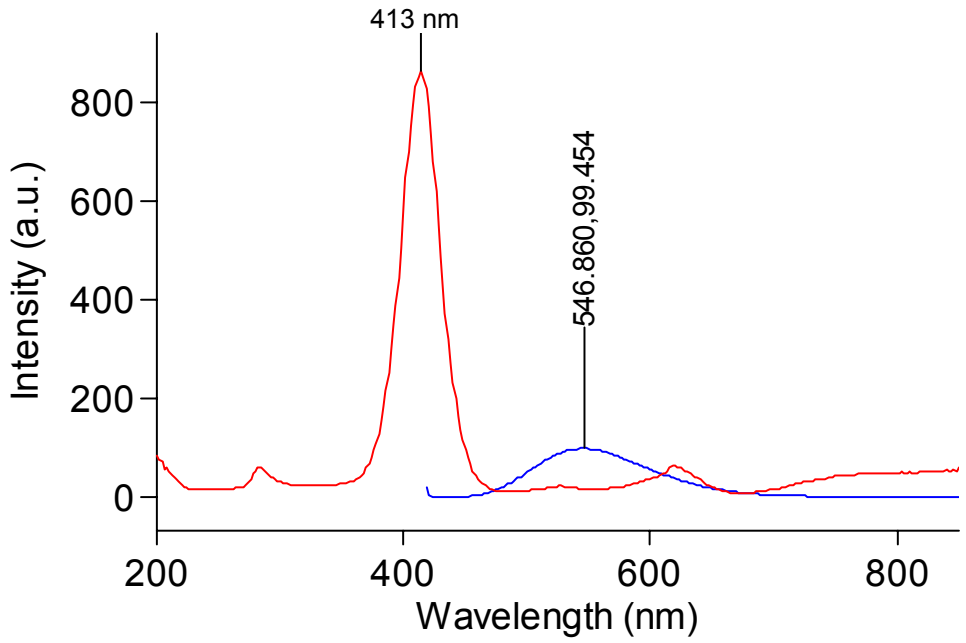

Figure S10. Absorption (red) and emission (blue) spectra for 5-{5'-(dimethylamino)-1-naphthalenesulfonamide-N-(2'-propynyl-1'-yl)}-2-hydroxypyrimdine (**2c**).

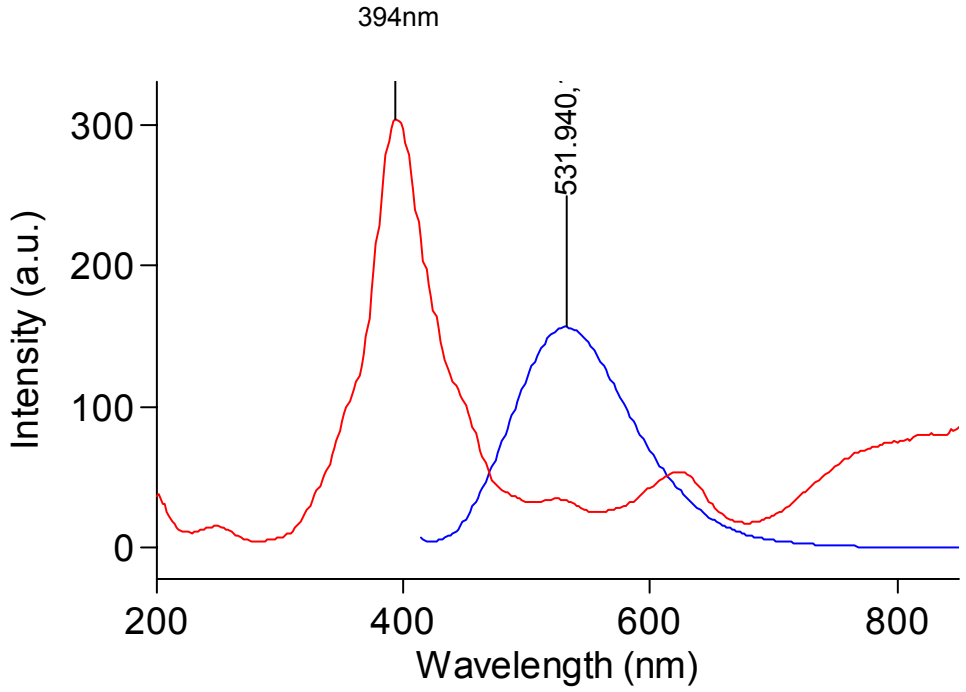

Figure S11. Absorption (red) and emission (blue) spectra for $[Pd_3(en)_3(4,7\text{-phen})_2(5\text{-}\{5'\text{-}(dimethylamino)\text{-}1\text{-}naphthalenesulfonamide\text{-}N\text{-}(2'\text{-}propynyl\text{-}1'\text{-}yl)\}pyrimidin\text{-}2\text{-}olate)](NO_3)_5$ (**3c**).