Supplementary Information to Communication

Facile Synthesis of an A_3B-type Phthalocyanine with a Peripheral Thiocatecholate Binding Group and its Coordination to Ni(dppe): Spectroscopy and Theory

Authors

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S1. General Comments

Methods and Materials

^1H and ^{13}C NMR spectra were obtained on a Bruker AVANCE 300 spectrometer. Chemical shifts are reported in δ (ppm) values. ^1H and ^{13}C NMR values were referenced to residual solvent as an internal standard, while ^{31}P NMR values were referenced to H_3PO_4 (external standard). The following abbreviations were used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad singlet. Mass spectra (MS) were recorded on either a Thermo Fischer Scientific LTQ-FT Ultra or on a Bruker Biflex III-Spectrometer. UV-Vis spectra were recorded on a Varian Eclipse. FTIR spectra were measured using a Bruker Alpha Platinum ATR single reflection diamond spectrometer. Quantum chemical calculations were performed using the MaRC2 computing cluster.

The following chemicals were used as received from their respective suppliers. 1,3-diiminoisoindoline and 1-iodomethane were purchased from Acros Organics. 4,5-dichlorophthalic acid and 2-Methyl-2-propanethiol was purchased from Sigma Aldrich. Carbon disulfide, 1,2-diamino-*ortho*-benzene and 1-iodobutane were purchased from Merck, dppe was purchased from Fluka and nickel dichloride hexahydrate was purchased from VWR Chemicals. Preparative silica TLC plates were purchased from Merck. 4,5-Dichlorophthalonitrile[1], 4,5-bis(*tert*-butylsulfanyl)benzene-1,2-dicarbonitrile[2] and 2-thione-benzimidazole[3] were synthesised according to literature procedures.

Theoretical Calculations

Geometries of **1** and **2** were first optimized in the gas phase at the B3LYP/6-31G(d,p) level of theory. Frequency calculations were then performed on the optimized structures at the same level of theory; no negative eigenvalues were obtained. TD-DFT calculations were also performed at the B3LYP/6-31G(d,p) level of theory solving for 20 states. All calculations were performed using the Gaussian09 suite of software.[4]

S2. Syntheses

*Synthesis of 4,5-bis(1H-benzimidazol-2-ylsulfanyl)benzene-1,2-dicarbo-nitrile (dbtpn) (**3**)*: 4,5-dichlorophthalonitrile (0.500 g; 2.54 mmol), 1,3-dihydro-2H-benzimidazole-2-thione (0.762 g; 5.07 mmol) and K_2CO_3(1.50 g; 10.85mmol) were mixed together and dissolved in DMF (10 ml). The solution was then warmed to 80 ºC for 3 h; reaction progress was monitored by TLC. H_2O was then added, and the precipitate that formed was collected by filtration, washed with H_2O and dried *in vacuo* (10^{-3} mbar). Mass: 0.960 g. Yield: 89 %. ^{1}H NMR (DMSO-*d6*; 300 MHz, 298 K): δ (ppm) 7.21-7.26 (m, 4H, benz); 7.54-7.59 (m, 4H, benz); 8.19 (s, 2H, phthalonitrile).^{13}C NMR(DMSO-*d6*; 75 MHz; 298 K): δ (ppm) 143.11; 149.54; 135.66; 122.60; 115.22; 113.91.

*Synthesis of 4,5-bis(1-butyl-benzimidazol-2-ylsulfanyl)benzene-1,2-dicarbonitrile (dBubtpn) (**4**)*: Dbtpn (0.900 g; 2.12 mmol) was dissolved in DMF (3 ml). NaOH(0.15 g) was crushed and added to this solution with stirring. After 5 minutes, 1-iodobutane (1.0 ml; 8.8 mmol) was added, and stirring was continued for 1 h. H_2O (50 ml) was then added, causing a very fine precipitate to form. The suspension was then extracted into DCM (3 x 50 ml). The organic portions were combined, dried ($MgSO_4$) and filtered. Volatiles were then evaporated to leave an oil, which was washed with hexane to leave a beige solid. Mass: 1.06 g. Yield: 93 %^{1}H NMR

(300 MHz; $CDCl_3$; 298 K): 0.85 (t, 6H, -CH_3); 1.17-1.29 (hex, 4H, -CH_2-); 1.69 (p, H, -CH_2-); 4.19 (t, 4H, -CH_2-); 7.28-7.40 (m, 6H, benzo); 7.63 (s, 2H, phthalonitrile); 7.73-7.76 (dd, 2H, benzo). MS(APCI+): Calcd for $C_{30}H_{29}N_6S_2$ $[M+H]^+$: 537.1890; Found: 537.1906.

Synthesis and quaternisation of asymmetrical (SR)$_2$PcH$_2$: dBubtpn (**4**) (1.05 g; 1.95 mmol) and 1,3-diiminoisoindoline (1.65 g; 11.40 mmol) were thoroughly ground together using a mortar and pestle before being added to a Schlenck tube. The mixture was then heated under N_2 with stirring for 6 h, during which time it forms a dark green paste. TLC analysis showed the presence of several colored products, but all were produced in trace amounts except for the two with the smallest R_f values. The paste was cooled to rt and then dissolved in EtOAc. This solution was filtered through a short silica gel column. Solvent was then removed to leave a blue-green solid, which was subsequently dissolved in DMF (10 ml). MeI (2.0 ml) were then added, and the solution was heated at 80 ºC in a sealed vessel for 12 h. The solution was then added to THF, and the solids that precipitated were collected by filtration and washed with THF. Solids were repeatedly dissolved in a minimal amount of DMF and precipitated with THF until the filtrate obtained from washing was colourless. Drying the precipitate *in vacuo* (10^{-3} mbar) left a blue-green coloured solid.

*Synthesis of [(dppe)Ni(S$_2$PcH$_2$)] (**1**)*: A degassed aqueous solution of NaOH was added to a portion of the blue-green solid obtained (0.200 g). The solution colour very quickly turns blue as the thiolate groups are formed/deprotected. The suspension was placed in an ultrasound bath for 30 min to ensure complete deprotection had taken place. This suspension was then added dropwise with vigorous stirring to a separately prepared solution of $NiCl_2$(dppe) (0.300 g ; 0.568 mmol) in THF (20 ml). The resulting suspension was then stirred at rt for 60 min before removing the solvent *in vacuo*. The residue was then extracted with $CHCl_3$ and filtered. The filtrate was concentrated and loaded onto a silica gel column. The product was eluted using DCM/EtOH (10:0.5) as the dark blue-green band. Mass: 0.085 g.Yield over three steps: 16.8 %. ^{1}H NMR (300 MHz; $CDCl_3$; 298 K): δ (ppm) = 2.53 (s, 4H, ethyl); 7.41-7.50 (m, 14H, Pc and Ph); 7.70 (m-br, 10 H, Pc and Ph).^{13}C NMR (75 MHz; $CDCl_3$; 298 K): δ (ppm) = 30.33 (ethyl), 125.51, 128.85 (t, J = 5.90 Hz, Ph), 130.83 (t, J = Hz, Ph), 132.08, 135.83, 151.52.^{31}P NMR (MHz; $CDCl_3$; 298 K): δ (ppm) = 33.26. MS(MALDI+): Calcd for $C_{56}H_{41}N_8NiP_2S_2$ ($[M+H]^+$): 1033.17; Found: 1033.17. FTIR: 508 (s); 533 (s); 688 (s); 733 (s); 1027 (m); 1101 (m); 1121 (m); 1176 (s); 1435 (m); 2850 (w); 2915 (w); 3054 (w). UV-Vis ($CHCl_3$): 777 (s); 718 (s); 693 (s); 656 (s); 341 (sh)

*Synthesis of (ButS)$_2$PcH$_2$ (**2**)*: 4,5-bis(*tert*-butylsulfanyl)benzene-1,2-dicarbonitrile(0.300 g; 0.985 mmol) and 1,3-diiminoisoindoline (0.575 g ; 3.96 mmol) were mixed together under N_2. The mixture was then heated at 200 ºC in a sealed vessel for 14 h. Once cool, the dark green mass was dissolved in DCM and loaded onto a silica gel column. The product was eluted used DCM and collected as the large dark blue band. Solvent was then evaporated and the dark blue solid remaining was washed with MeOH before being dried *in vacuo* (10^{-3} mbar). ^{1}H NMR (300 MHz; CD_2Cl_2; 298 K): 1.26 (s, 18H, -CH_3); 7.00-8.06 (m, 14H, Pc). MS (APCI+):Calcd for $C_{40}H_{35}N_8S_2$ $[M+H]^+$: 691.2421; Found: 691.2442.UV-Vis (DCM): 690 (s), 664 (s), 638 (s), 607 (sh)

S3. FTIR Spectra

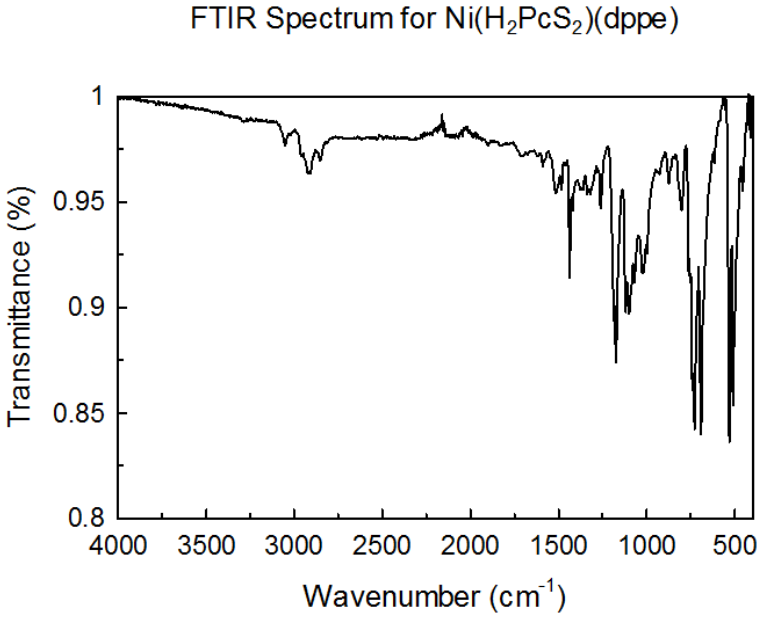

Figure S1. FTIR Spectrum for **1.**

S4. UV-Vis Spectra

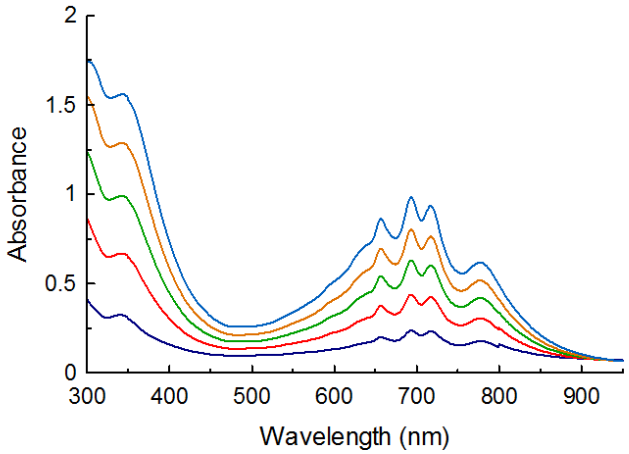

Figure S2. UV-Vis Spectra for **1** at increasing concentration to determine **1**'s molar attenuation coefficient.

S5. NMR Spectra

All NMR spectra were recorded in $CDCl_3$ at room temperature.

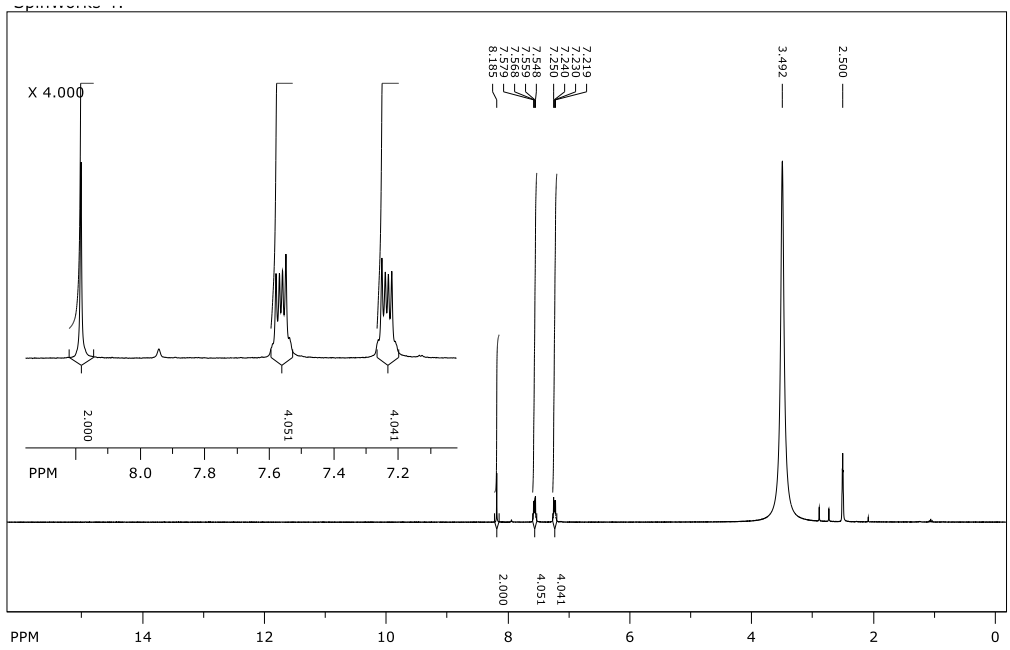

Figure S3. ^{1}H NMR Spectrum of **3**

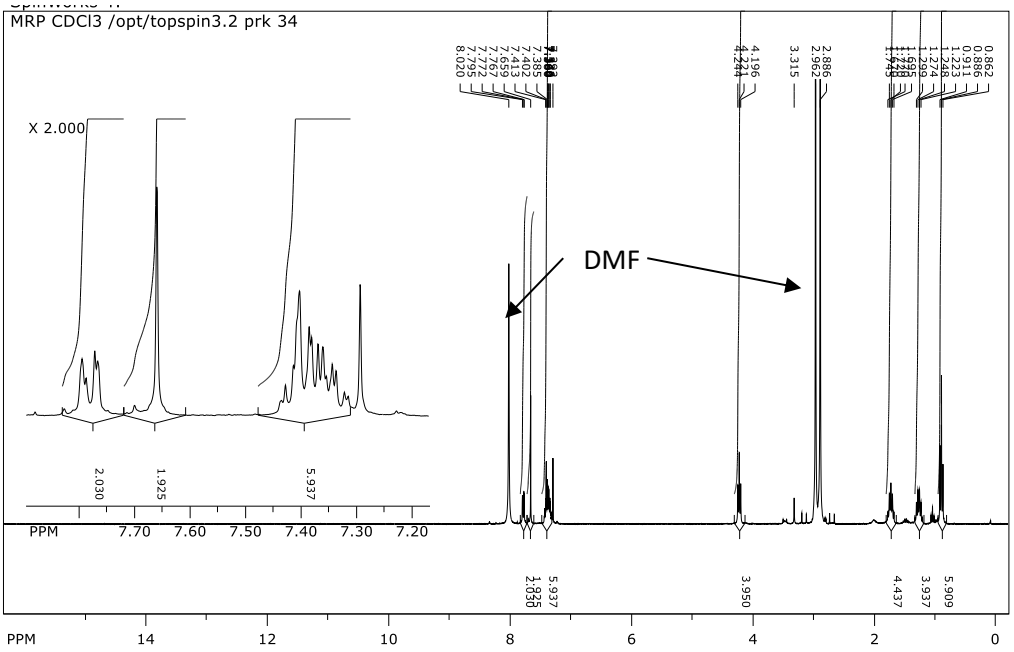

Figure S4. [1]H NMR Spectrum of **4**

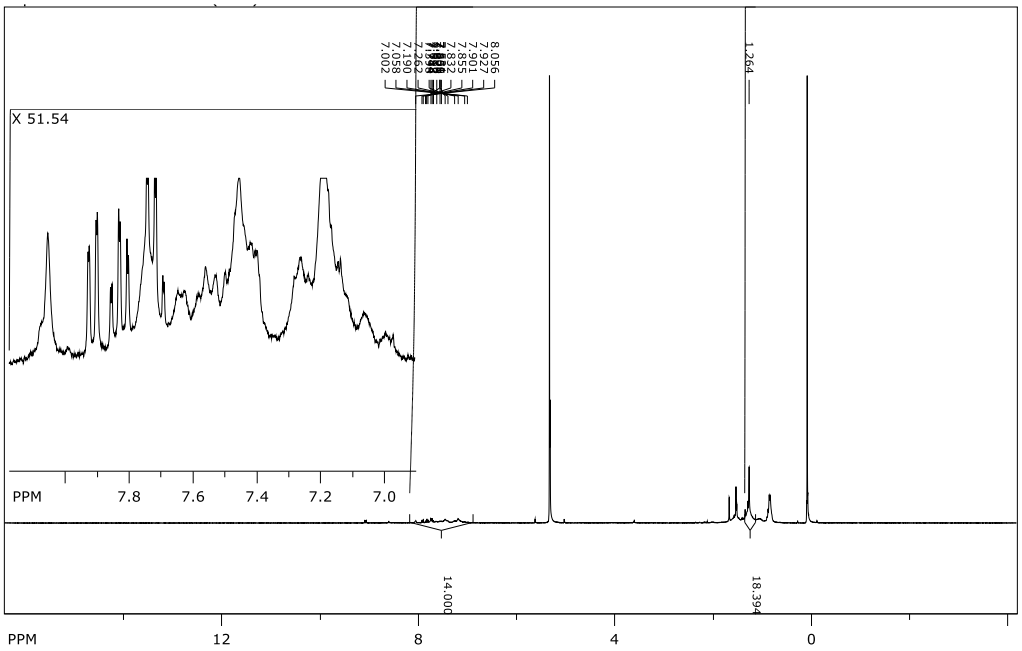

Figure S5. [1]H NMR Spectrum of **2**

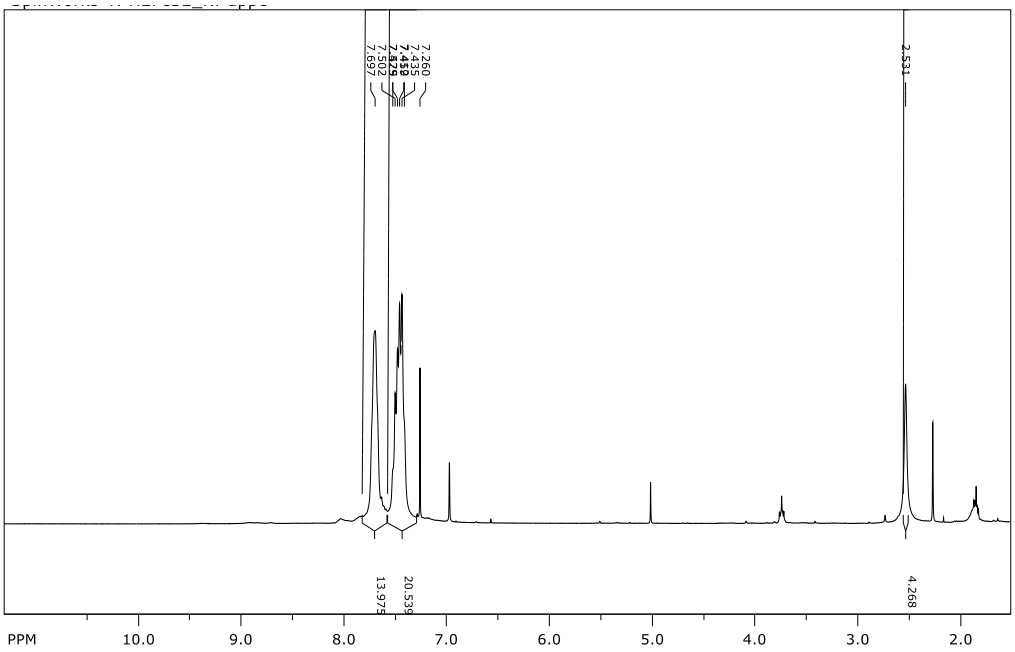

Figure S6. ^{1}H NMR Spectrum of **1**

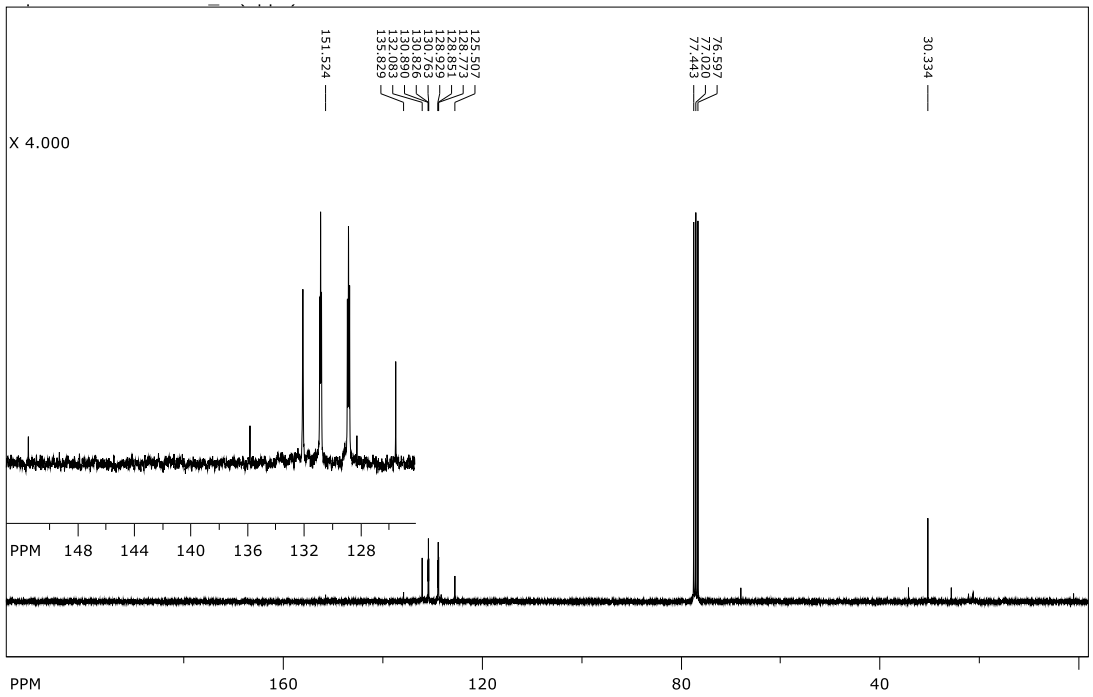

Figure S7. ^{13}C NMR Spectrum of **1**

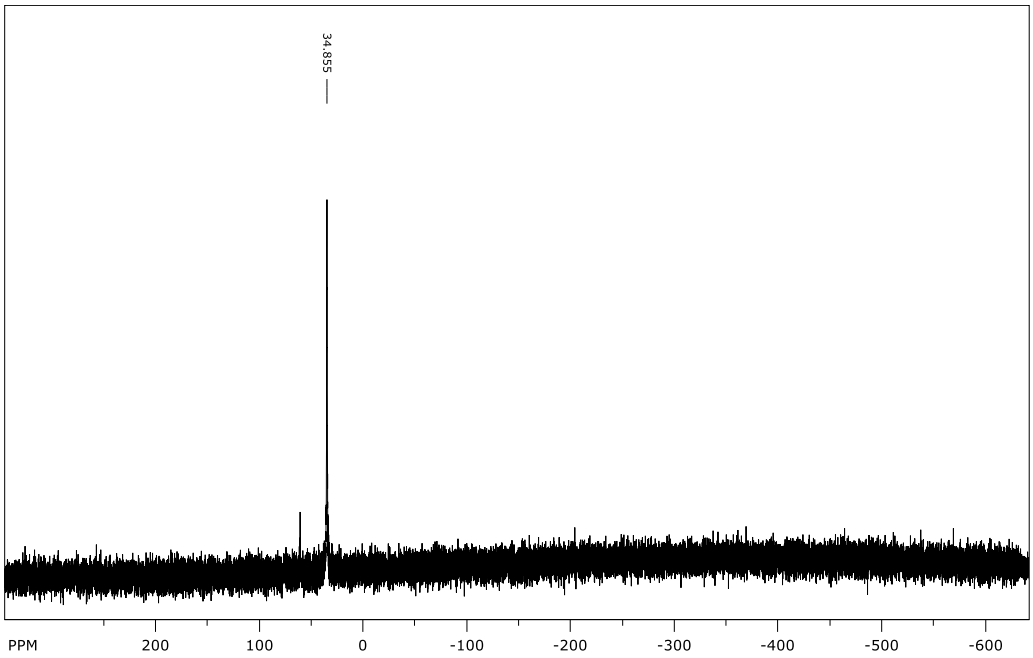

Figure S8. ^{31}P NMR Spectrum for **1**

S6. Mass Spectrometry

MALDI-TOF MS for Ni(H_2PcS_2)(dppe) (**1**)

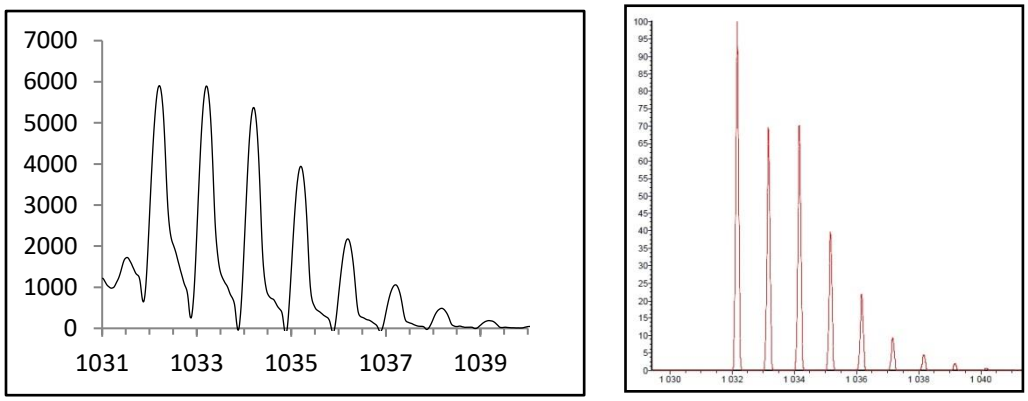

Figure S9. Found (left) and calculated (right) MALDI-TOF MS spectra for **1**.

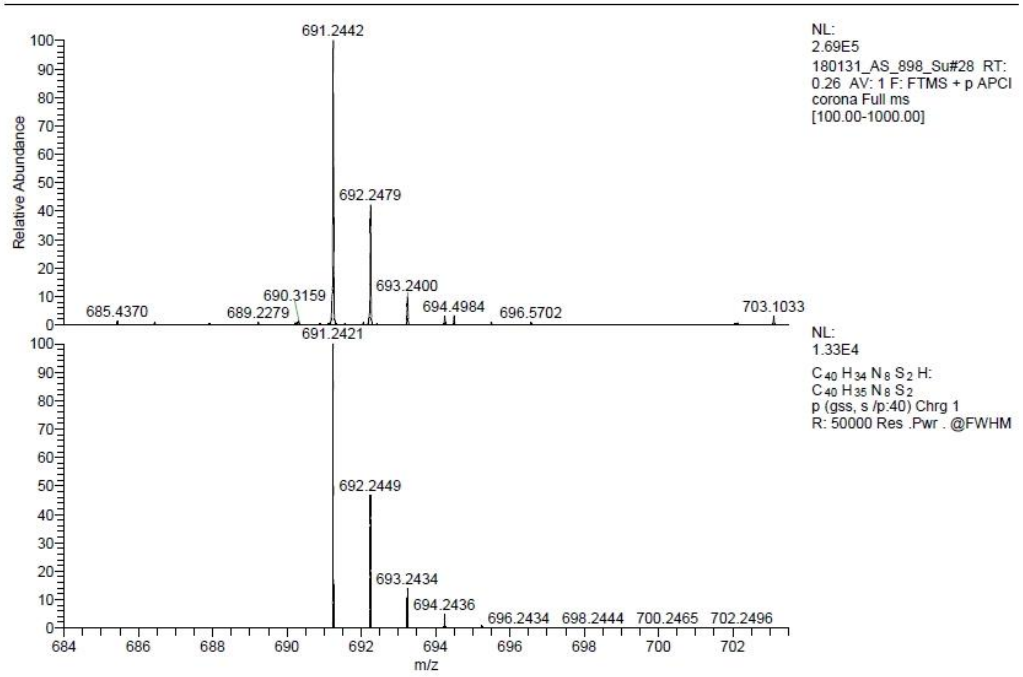

Figure S10. Found (top) and calculated (bottom) MS(APCI+) Spectra for **2**.

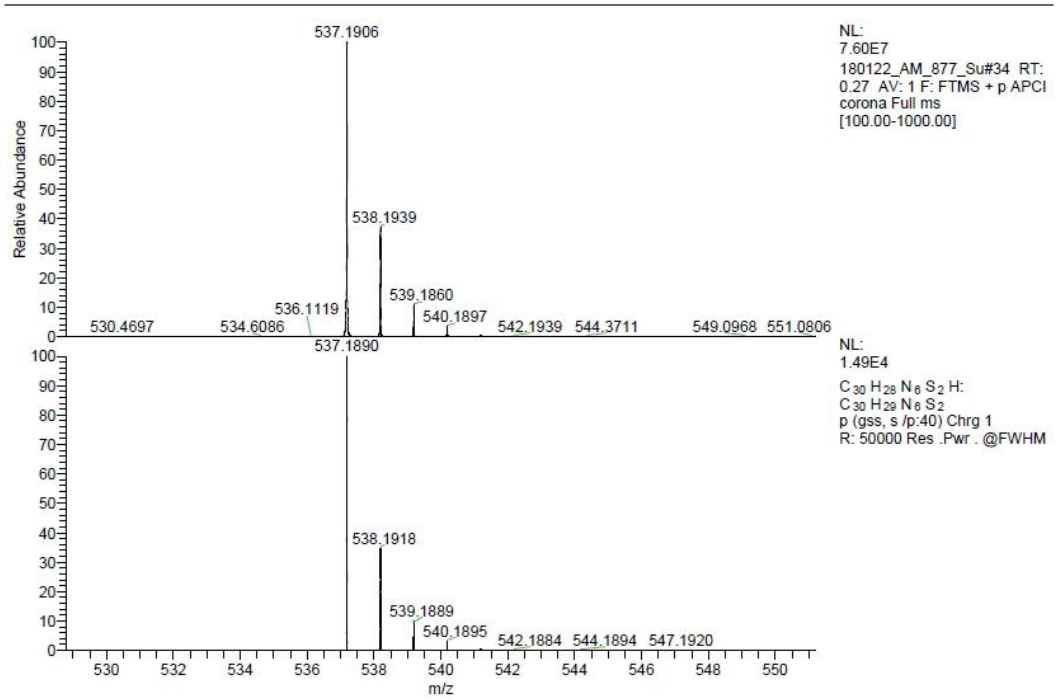

Figure S11. Found (top) and calculated (bottom) MS(APCI+) Spectra for **3**.

S7. MOs for $H_2Pc(SMe)_2$ (2)

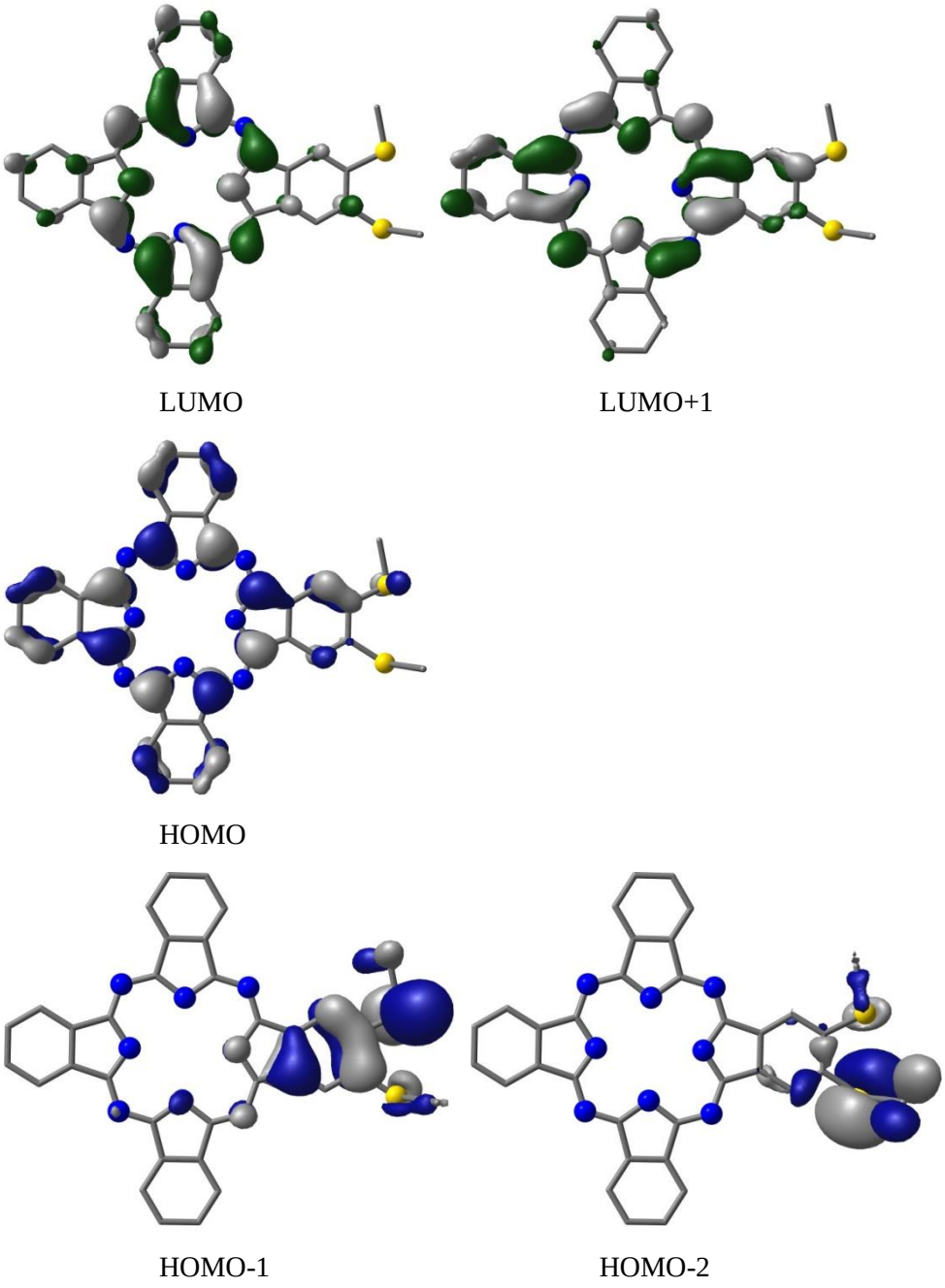

Figure S12. LUMO (top left), LUMO+1 (top right), HOMO (middle), HOMO-1 (bottom left) and HOMO-2 (bottom right) for the ligand $(MeS)_2PcH_2$.

S8. References

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4 Gaussian 09, Revision C.01, 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, T. Keith, 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, 2010.