Electronic Supplementary Material (ESI) for Chemical Communications

Unexpected formation of the nickel *seco*-tribenzoporphyrazine with a tribenzotetraazachlorin-type absorption spectrum

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Supporting Information

Experimental Section

Reagents and materials. All reactions were performed under an argon atmosphere using standard Schlenk techniques. 1,3-diiminoisoindoline, 5,6-bis(octyloxy)-1,3-diiminoisoindoline, and nickel acetate were purchased from Aldrich and used without further purification. 2,5-Diamino-3,4-dicyanothiophene was prepared using literature method.[1] Silica gel (60 Å, 60-100 μm) and high-performance TLC plates were purchased from Dynamic Adsorbents Inc. Size-exclusion chromatography was conducted using SX-1 Bio-beads purchased from Bio-Rad Inc. N,N-Dimethylaminoethanol was purchased from Acros and used without further purification.

Spectroscopy Measurements. UV-Vis data were obtained on Jasco-720 or Cary 17 spectrophotometers. MCD data were recorded using OLIS DCM 17 CD spectropolarimeter with a 1.4 T DeSa magnet. The MCD spectra were measured in mdeg = [θ] and converted to Δε (M^{-1} cm^{-1} T^{-1}) using the regular conversion formula: $\Delta\varepsilon=\theta/(32980 \bullet Bdc)$, where B is the magnetic field, d is the path length, and c is the concentration. Complete spectra were recorded at room temperature in parallel and anti-parallel directions with respect to the magnetic field. NMR spectra were recorded on a Varian INOVA instrument with a 500 MHz frequency for protons or JEOL instrument with a 400 MHz frequency for protons. Chemical shifts are reported in parts per million and referenced to TMS as an internal standard. APCI and APCI MS/MS spectra were recorded using Agilent ESI/APCI LC/MS system, while MALDI-TOF spectra were obtained on PerSeptive Biosystem instrument. Elemental analyses were conducted by analytical center at Tohoku University.

DFT-PCM and TDDFT-PCM Calculations. For the sake of simplicity, in all calculations, peripheral *tert*-butyl groups in *seco*-porphyrazine **4** were replaced by the hydrogen atoms. The initial geometries of *seco*-porphyrazine **4** were restrained in C_s (planar macrocycle) and C_2 (non-planar macrocycle) point groups. Geometry optimizations were conducted for both point groups using the polarized continuum model (PCM) approach[2] and DCM as a solvent. Converged geometries were tested by frequency calculations in order to confirm the nature of stationary points. It was found that the planar C_s geometry has one negative frequency, which transforms planar macrocyclic core into non-planar one. Optimized non-planar C_2 point group geometry, on the other hand, was confirmed to be a stationary minimum point judged by the absence of the imaginary frequencies. Thus, only non-planar C_2 point group geometry was used for single-point and TDDFT calculations. All geometry optimizations, single-point DFT-PCM and TDDFT-PCM calculations were conducted using a pure BP86 functional.[3] The first 50 states were considered in all PCM-TDDFT calculations. In all cases, 6-31G(d) basis set was used for all atoms.[4] All calculations were performed using Gaussian 09 software.[5] TDDFT predicted UV-vis spectra profiles were modeled using GaussView software[6] and 800 cm^{-1} bandwidth for all bands. Molecular orbital analysis was conducted using the QMForge program.[7]

Preparation of seco-porphyrazines **4** and **5.** Mixture of 2,5-diamino-3,4-dicyanothiophene (**3**) (820 mg; 5 mmol) and 5-*tert*-butyl-1,3-diiminoisoindoline (1 g; 5 mmol) was refluxed in 15 ml of N,N-dimethylaminoethanol in the presence of $Ni(OAc)_2 \times 6H_2O$ (1.2 g, 5 mmol) for 24 h under argon atmosphere. After this period of time, a solution was poured into water, filtered, washed with water, methanol, and dried under vacuum. The residue was dissolved in chloroform and purified on silica gel column using first chloroform, and then chloroform-ethanol (7:3 v/v) as eluents. The second deep blue fraction was collected and purified by using size-exclusion chromatography (Bio-beads, SX-1 column), and then preparative TLC (SiO_2, chloroform-ethanol 8:2 v/v as eluent). Analytically pure sample was obtained after precipitation of chloroform solution of **4** by ethanol. Yield: 5.6 mg (0.5 %). Mp > 250 ^{0}C. ^{1}H NMR (ppm, $CDCl_3$): 10.06-9.89 (m, 2H, *seco*-H), 8.72-8.39 (m, 6H, α-Pc), 7.94-7.83 (m, 3H, β-Pc), 1.78-1.72 (m, 27H, *tert*-Bu). UV-vis (λ, nm (log ε), DCM): 268 (4.79), 285 (4.81), 333 (4.63), 361sh, 416 (3.87), 553 sh, 596 (4.69), 662 (4.22), 695 (4.4), 727 (5.1). IR (cm^{-1}, KBr): 3070 (Ar-H), 2957 (C-H, t-Bu), 1616, 1543, 1482, 1395, 1364, 1321, 1283, 1258, 1204, 1163, 1142, 1103, 1088, 938, 828, 747. Elemental analysis: Found: C, 66.64; H, 6.08; N, 15.85; S, 0.00%; Calculated for $C_{38}H_{38}N_8Ni\cdot H_2O$: C, 66.76; H, 5.86; N, 16.40; S, 0.00%. MS (FAB$^+$, *m*-nitrobenzyl alcohol, APCI, THF, *m/z*) $[M+H]^+$ 665 (100%). The first fraction purified by column chromatography was found to be a symmetric phthalocyanine **6.** Yield: 672 mg (68%). We did not attempted to identified the insoluble in chloroform brown residue, which most likely consists of initial thiophene **3** and oligomeric open-chain reaction by-products.

In attempt to separate individual positional isomers of *seco*-porphyrazine **4**, it was loaded on the high-performance TLC plates and eluted with DCM-ethanol (9:1 v/v). Two fractions were separated. The first fraction has ^{1}H NMR spectrum of pure isomer **4a** or **4b**, while the second fraction was a mixture of the remaining isomers. ^{1}H NMR (ppm, $CDCl_3$): 10.39 (s, H, *seco*-H), 10.35 (s, H, *seco*-H), 8.98 (d, J = 8 Hz, 2H, α-Pc), 8.89 (s, 1H, α-Pc), 8.81 (d, J = 8 Hz, 1H, α-Pc), 8.73 (d, J = 8 Hz, 1H, α-Pc), 8.61 (d, J = 8Hz, 1H, α-Pc), 8.02 (m, 2H, β-Pc), 7.95 (d, 8Hz, 1H, β-Pc), 1.77 (s, 9H, *tert*-Bu), 1.74 (s, 9H, *tert*-Bu), 1.73 (s, 9H, *tert*-Bu).

Similarly to preparation of *seco*-porphyrazine **4**, mixture of 2,5-diamino-3,4-dicyanothiophene (**3**) (164 mg; 1 mmol) and 5,6-bis(octyloxy)-1,3-diiminoisoindoline (400 mg; 1 mmol) was refluxed in 15 ml of N,N-dimethylaminoethanol in the presence of $Ni(OAc)_2$ x $6H_2O$ (284 mg, 1 mmol). After similar to mentioned above reaction mixture work-up, 1.3 mg (0.3 %) of *seco*-porphyrazine **5** was isolated. ^{1}H NMR (ppm, $CDCl_3$): 9.62 (br s, 2H, *seco*-H_a), 8.02 (s, 2H, α-Pc), 7.90 (s, 2H, α-Pc), 7.75 (s, 2H, α-Pc), 4.84 (br s, 4H, 1-CH_2), 4.41 (br s, 4H, 1-CH_2), 4.27 (br s, 4H, 1-CH_2), 2.16 (br m, 12H, 2-CH_2), 1.76-1.26 (br m, 60H, 3-7-CH_2), 0.98 (br s, 18H, 8-CH_3). Electronic spectrum (λ, nm (log ε), DCM): 290 (5.07), 333 (4.69), 371 (4.57), 430 (4.28), 553 sh, 596 (4.79), 667 (4.41), 696 (4.6), 727 (5.14). MS (MALDI-TOF$^+$, dithranol, *m/z*) $[M+H]^+$ 1266 (100%). Yield of symmetric phthalocyanine **7** was 223 mg (56%).

References:

1. W. J. Middleton, V. A. Engelhardt, B. S. Fisher, *J. Am. Chem. Soc.*, 1958, **80**, 2822.
2. Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.*, **2005**, *105*, 2999-3093.
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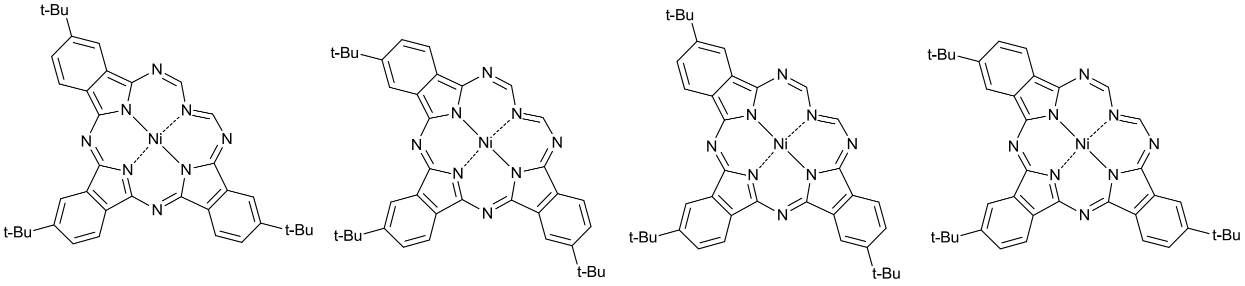
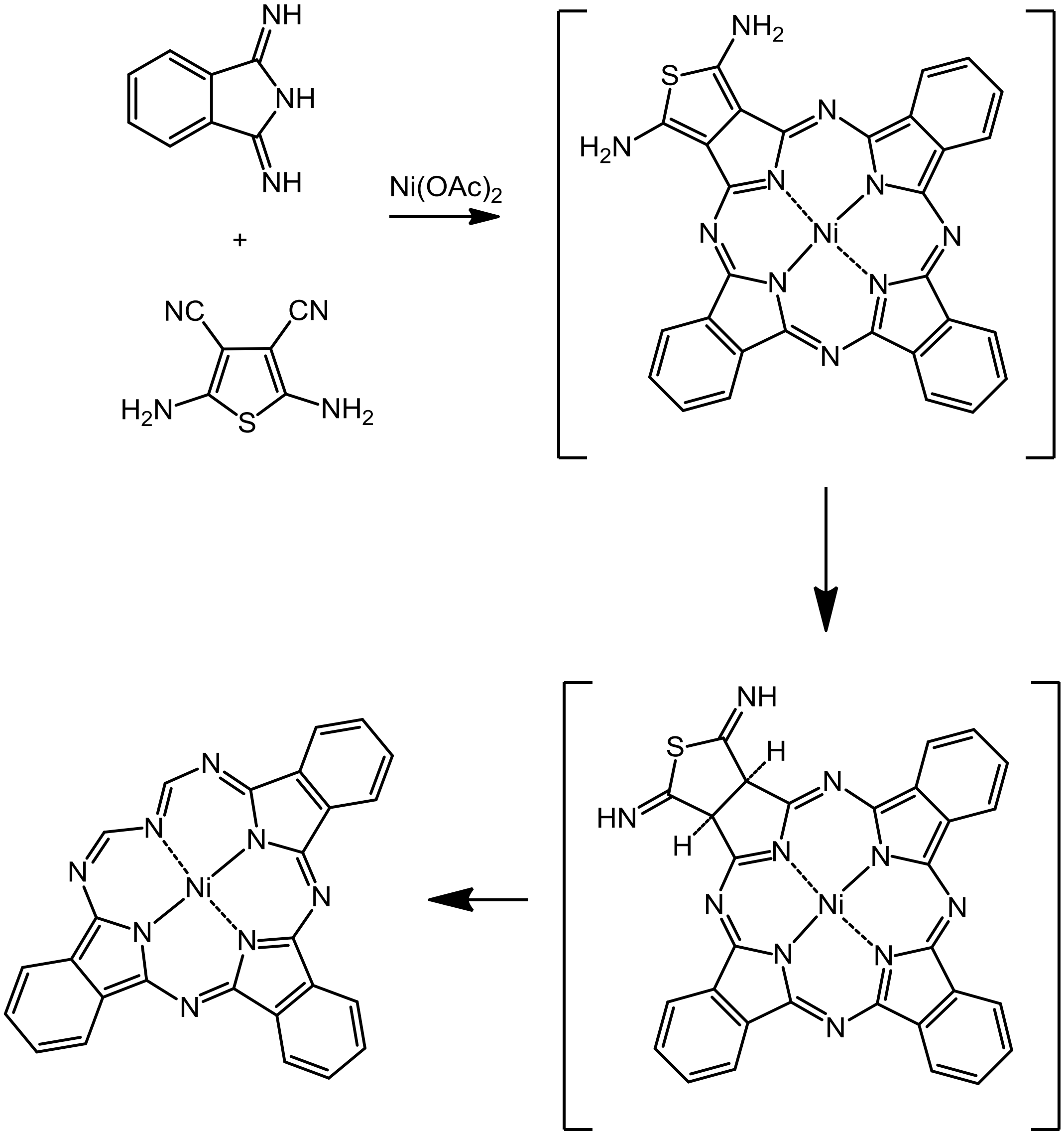
Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

6. GaussView 5.0. Gaussian, Inc., Wallingford CT, 2009.
7. Tenderholt, A. L. *QMForge, Version 2.1.* Stanford University, Stanford, CA, USA.

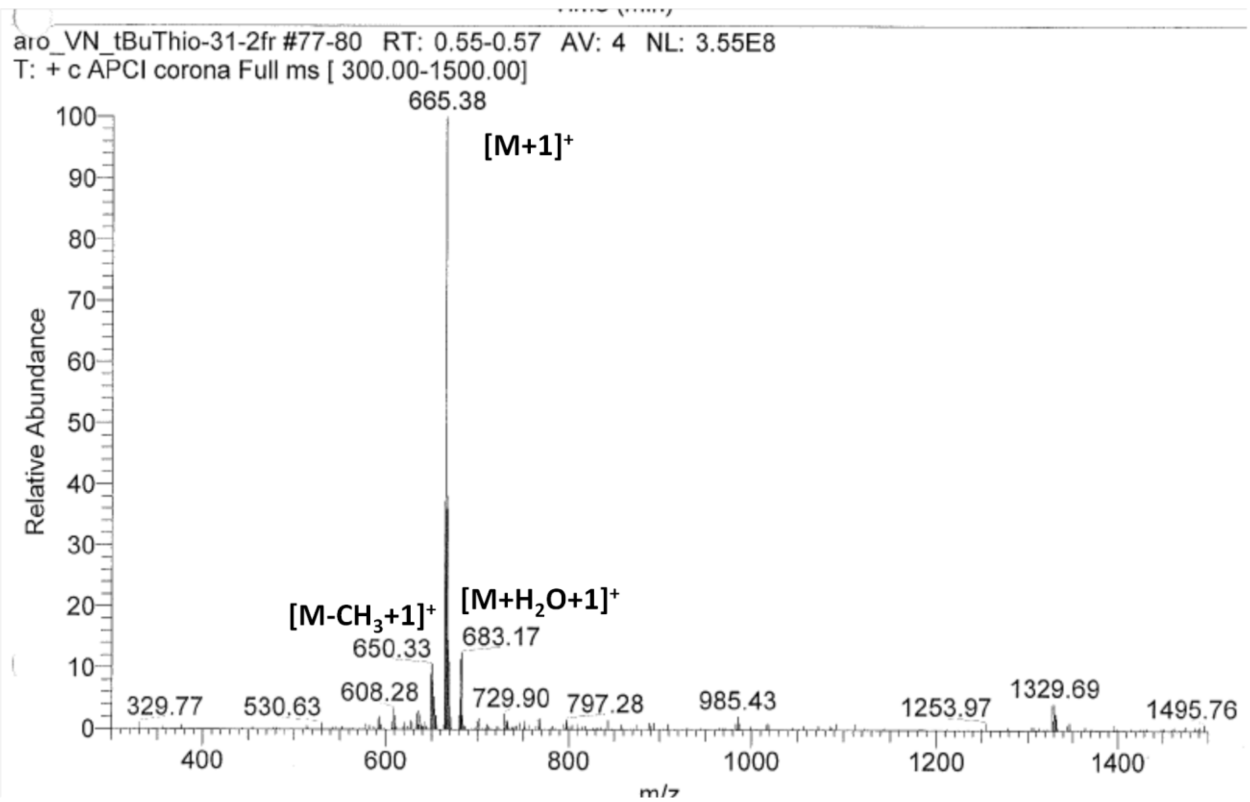


4a **4b** **4c** **4d**

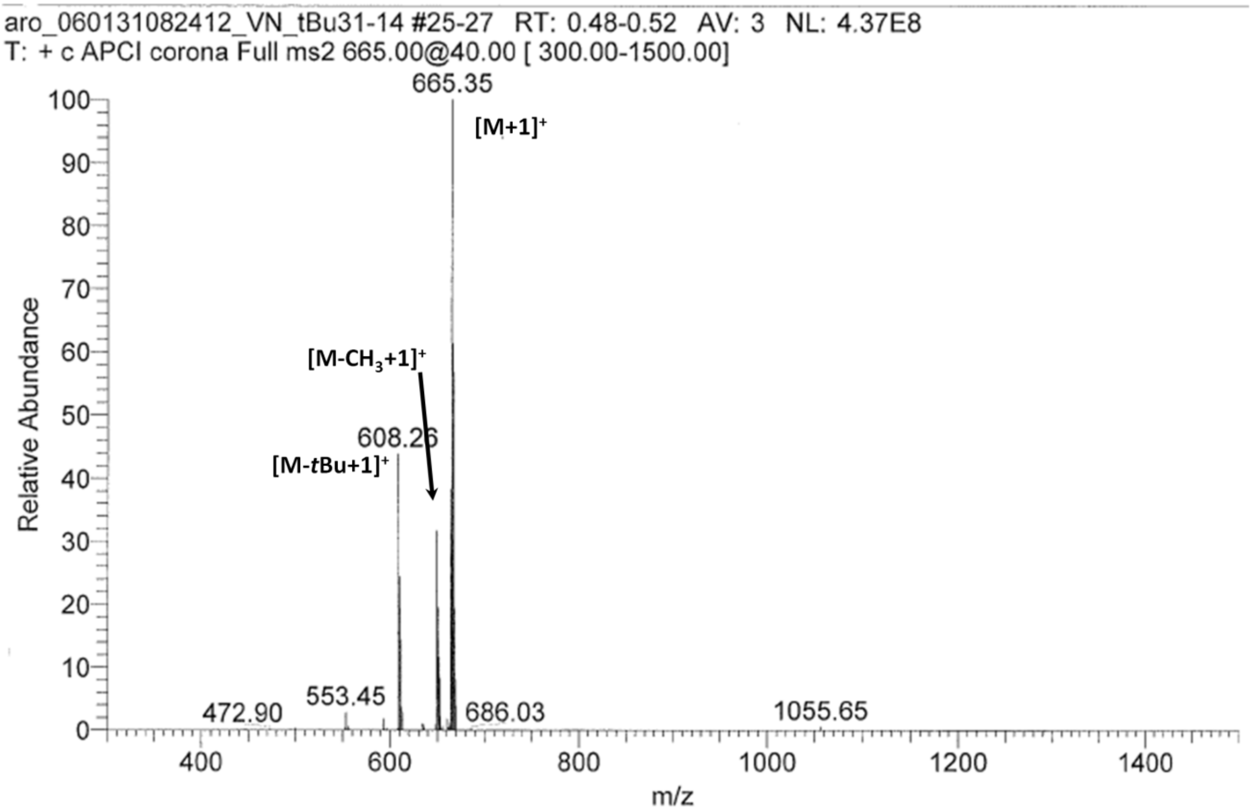
Supporting Information Figure 1. Positional isomers of *seco*-porphyrazine **4**.



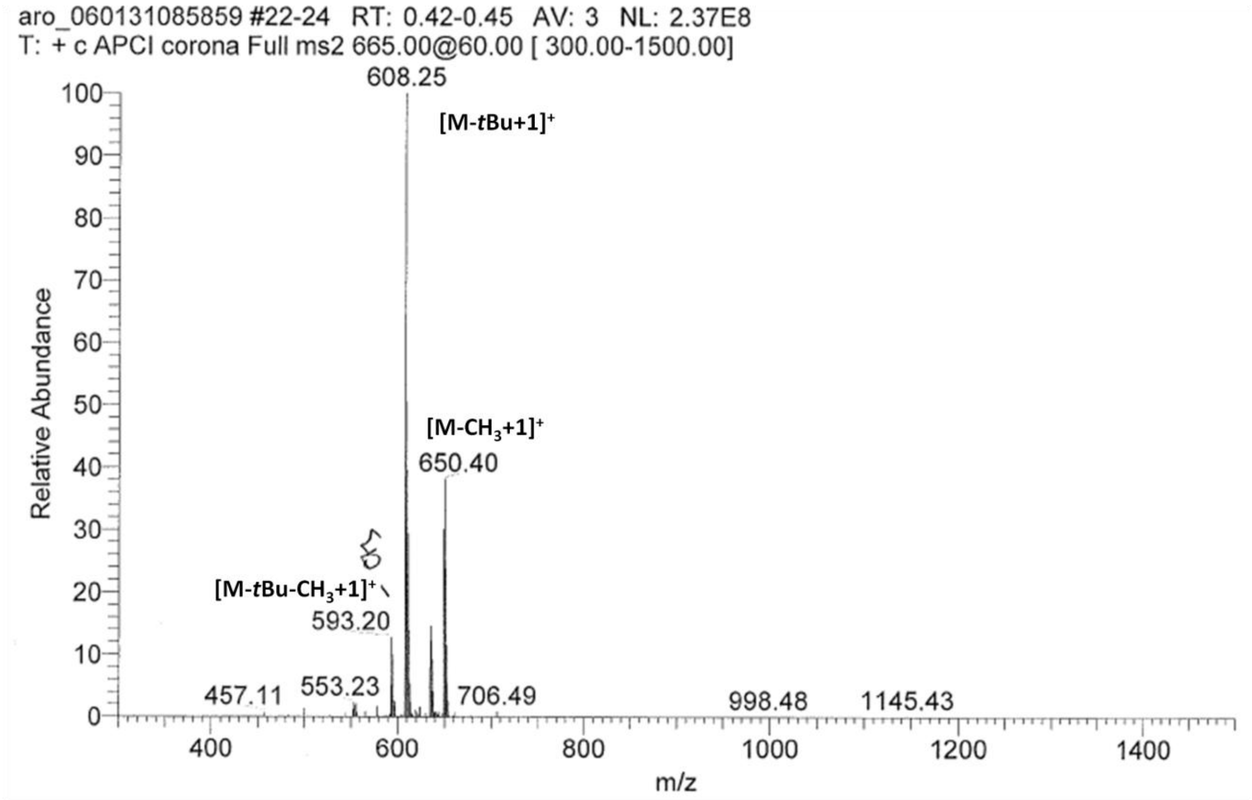
Supporting Information Scheme 1. One of the possible mechanisms for the formation of *seco*-porphyrazines **4** and **5**.



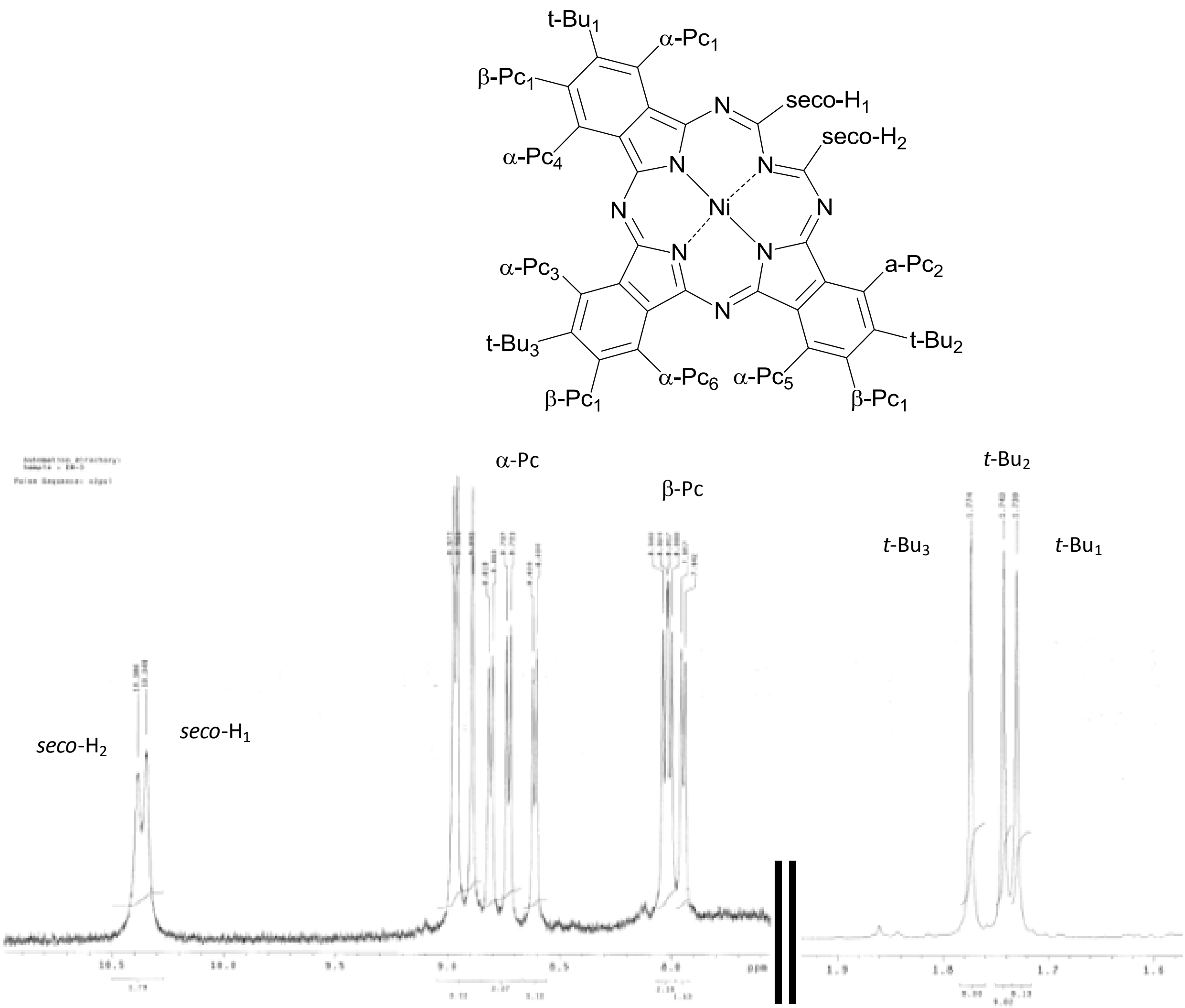
Supporting Information Figure 2. APCI mass spectrum of *seco*-porphyrazine **4** in THF.



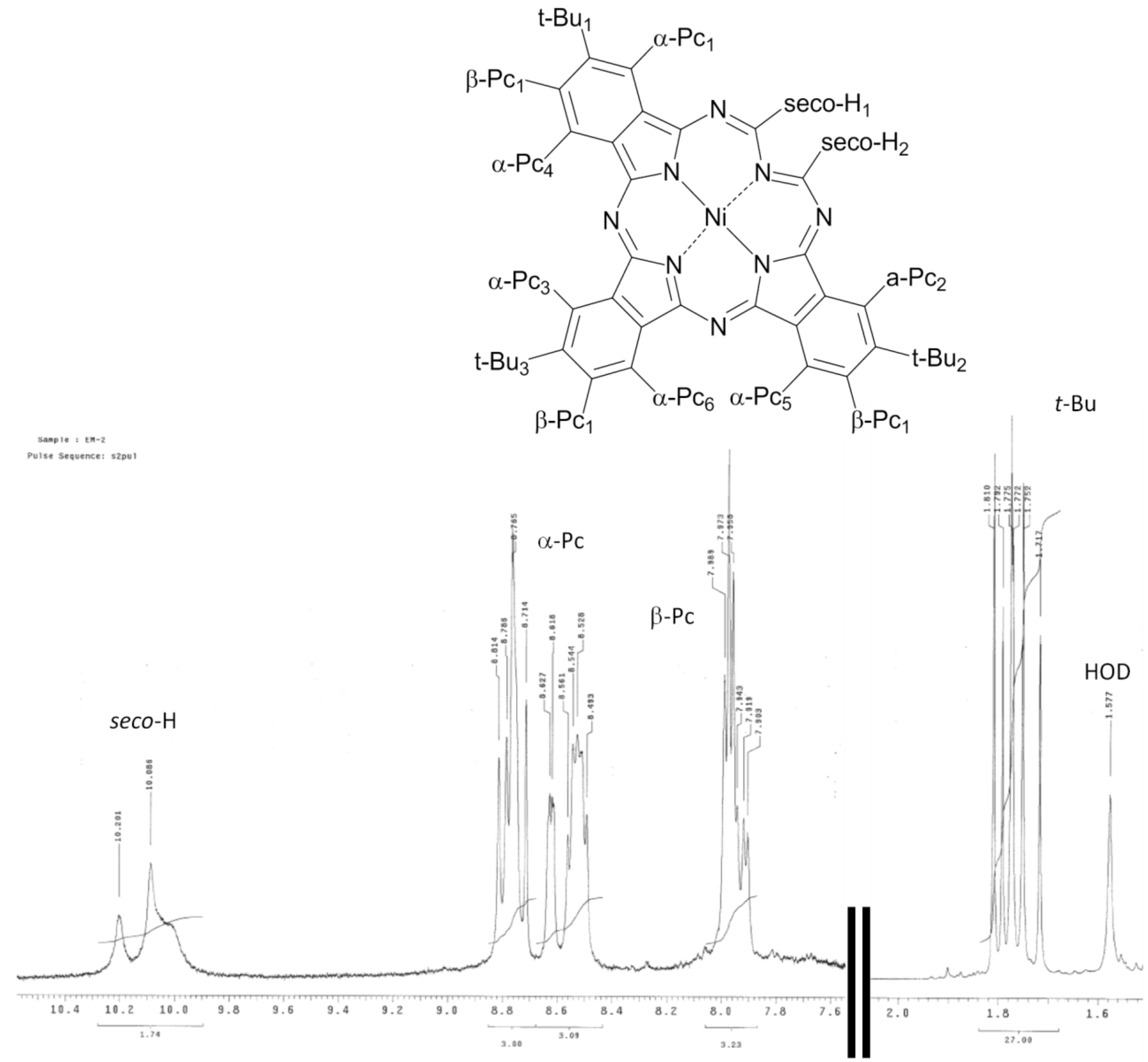
Supporting Information Figure 3. APCI mass spectrum of *seco*-porphyrazine **4** in THF at 40% collision energy.



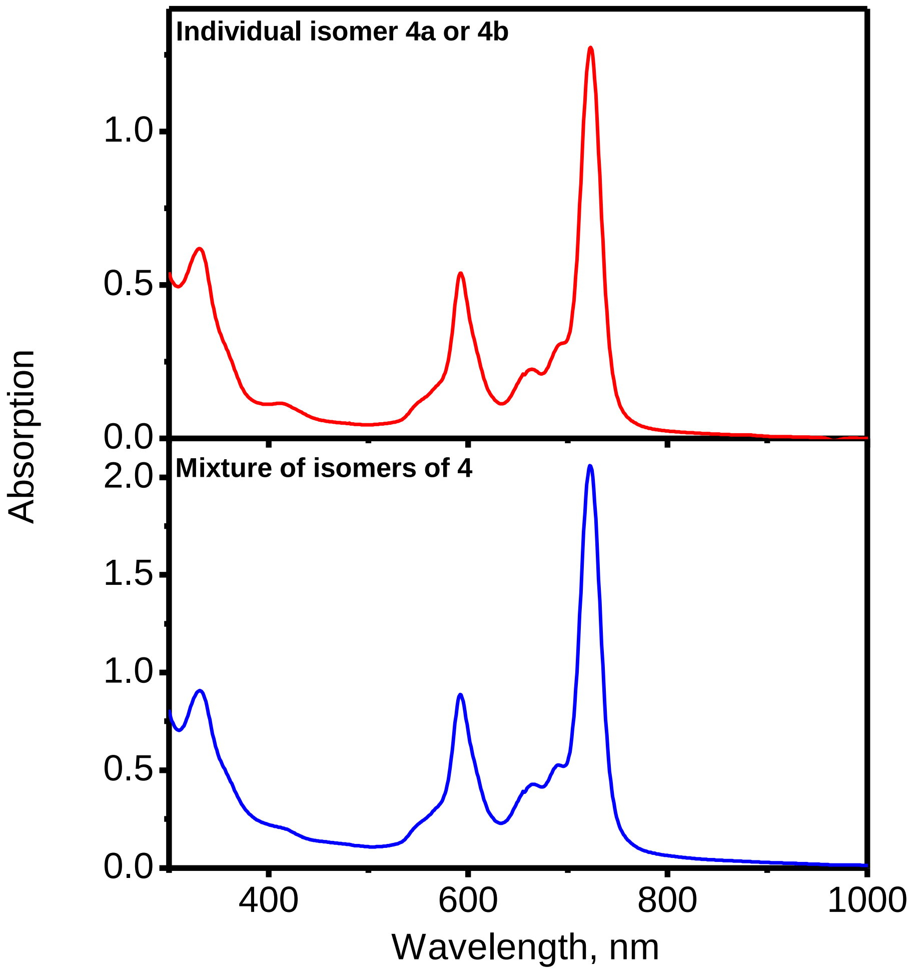
Supporting Information Figure 4. APCI mass spectrum of *seco*-porphyrazine **4** in THF at 60% collision energy.



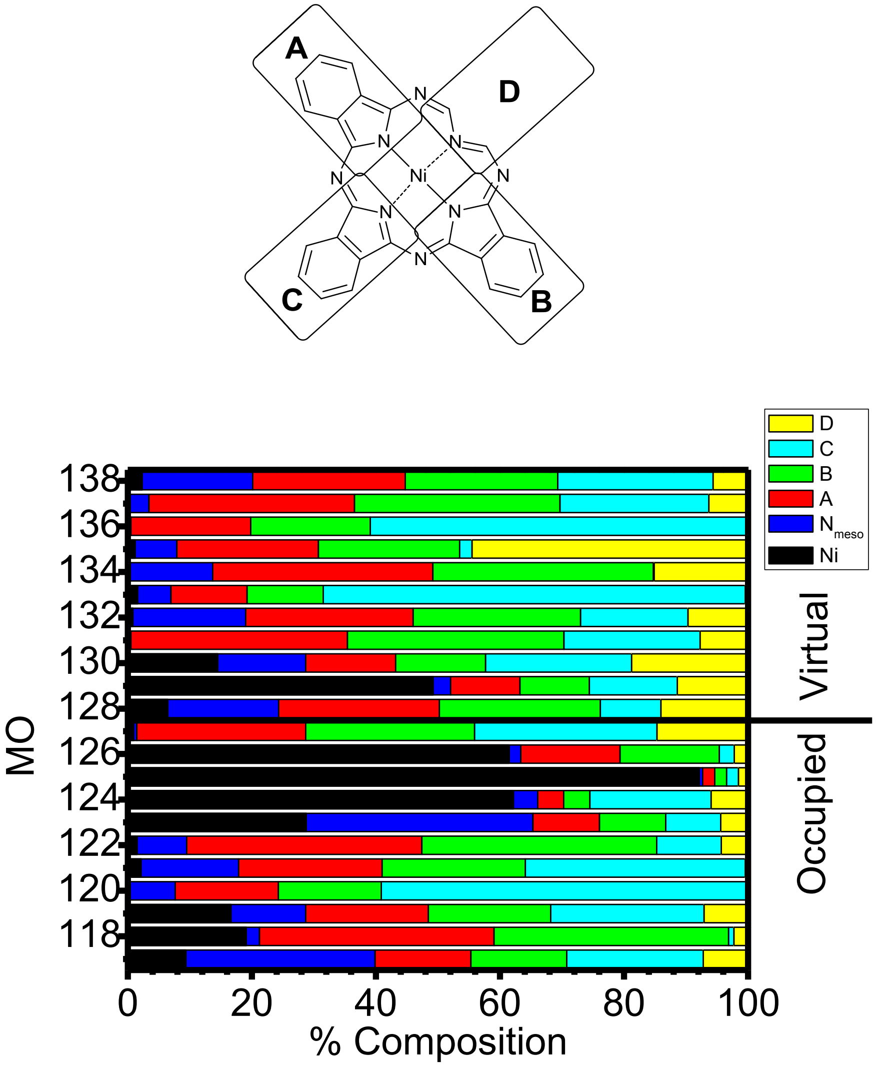
Supporting Information Figure 5. ^{1}H NMR spectrum of *seco*-porphyrazine **4a** or **4b** in $CDCl_3$.



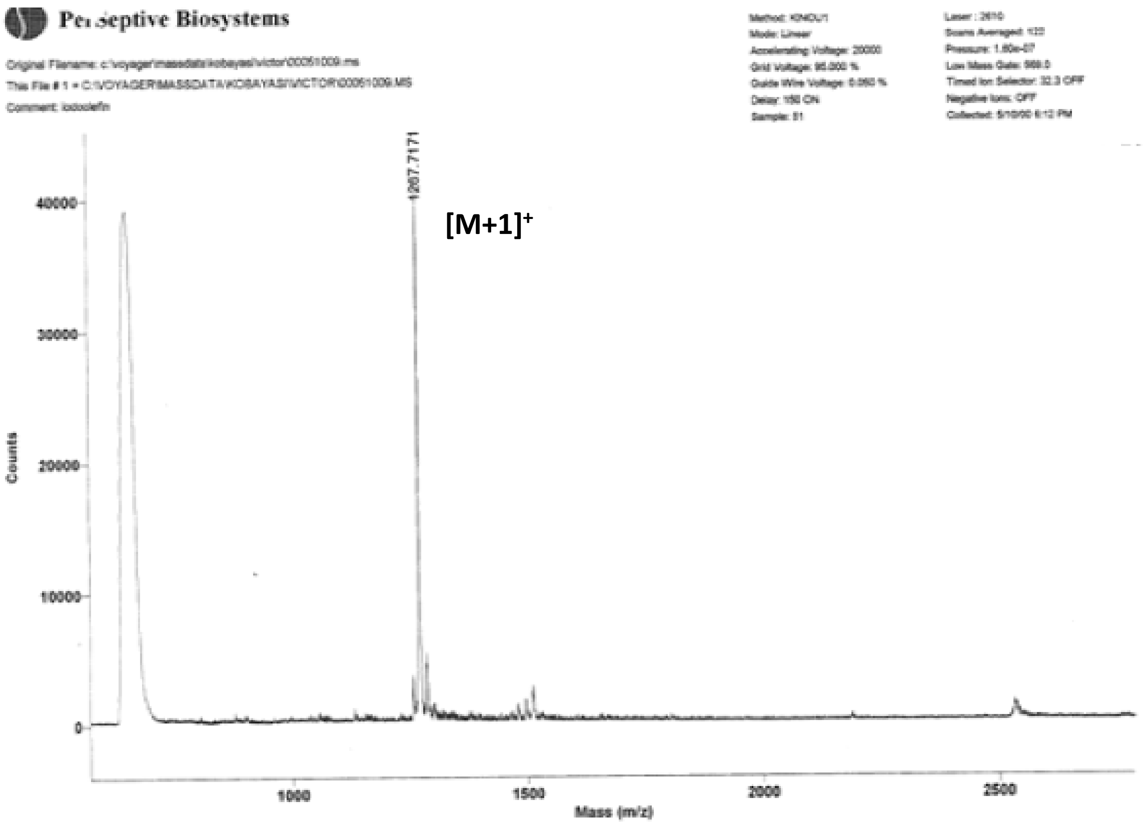
Supporting Information Figure 6. ^{1}H NMR spectrum of *seco*-porphyrazine **4** (mixture of positional isomers) in $CDCl_3$.



Supporting Information Figure 7. UV-vis spectra of individual isomer **4a** or **4b** and the mixture of isomers of *seco*-porphyrazine **4** in DCM.



Supporting Information Figure 8. PCM-DFT predicted molecular orbital compositions of *seco*-porphyrazine **4**.



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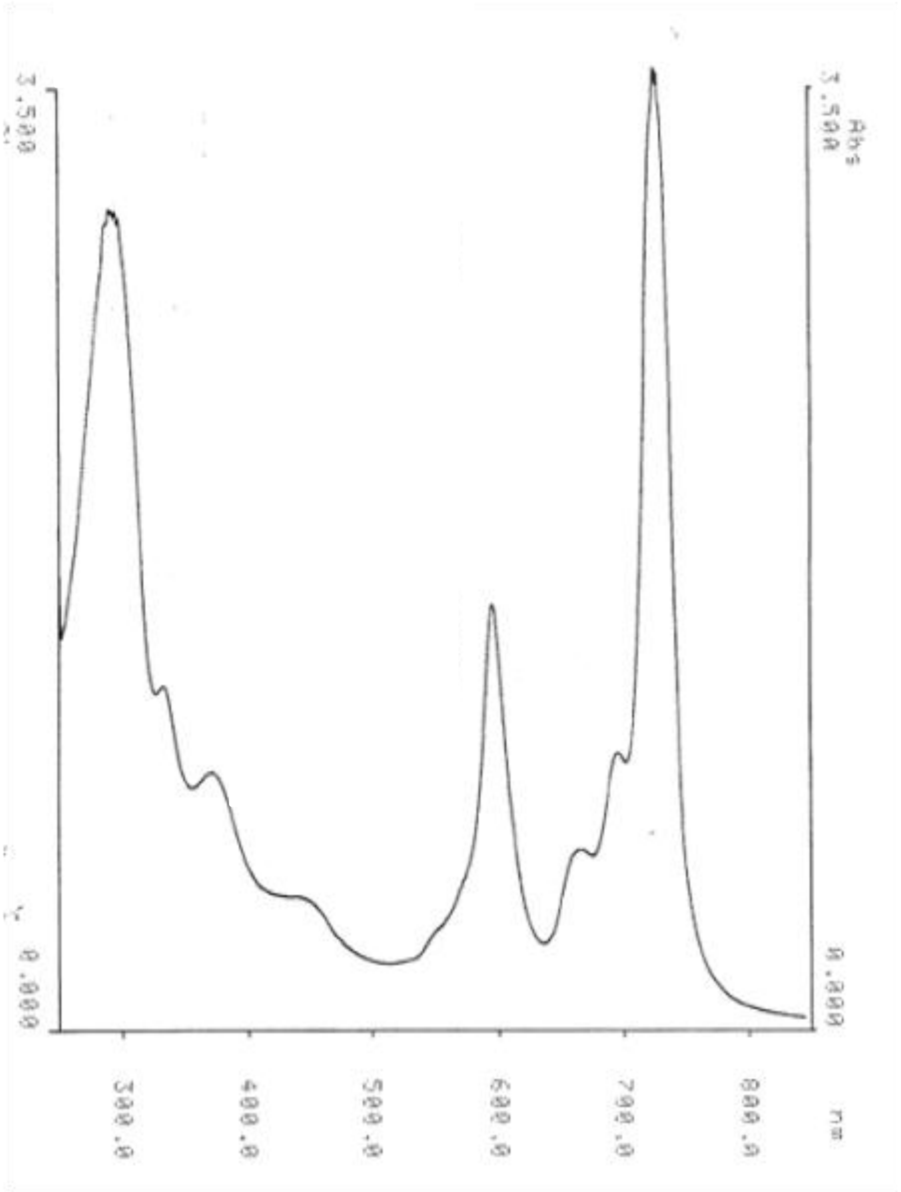
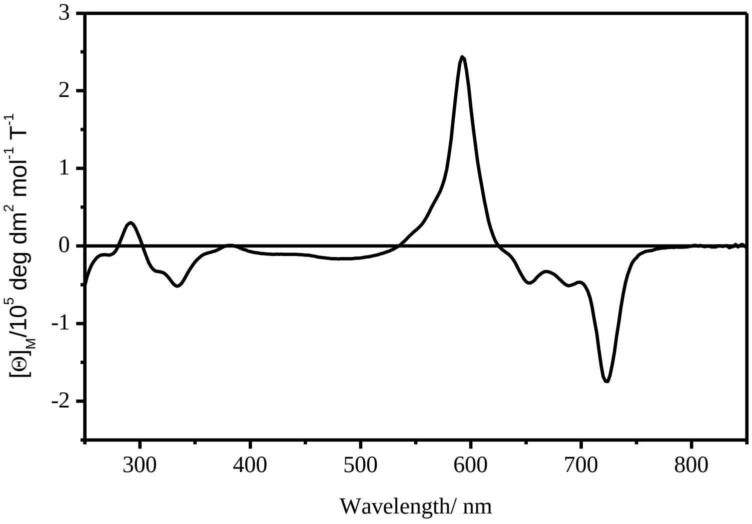
Supporting Information Figure 9. MALDI-TOF spectrum of *seco*-porphyrazine **5**.



Supporting Information Figure 10. UV-vis spectrum of *seco*-porphyrazine **5**.



Supporting Information Figure 11. MCD spectrum of *seco*-porphyrazine **5**.

Optimized Coordinates of nickel *seco*-porphyrazine **4** at PCM BP86/6-31G(d) level:

N	0	0	-1.06733
C	0.15964	1.10424	-1.90239
C	-0.15964	-1.10424	-1.90239
C	0.11785	0.69647	-3.29771
C	-0.11785	-0.69647	-3.29771
C	0.23309	1.41683	-4.49881
C	-0.23309	-1.41683	-4.49881
C	0.11526	0.69958	-5.69728
C	-0.11526	-0.69958	-5.69728
N	-0.10842	1.88078	0.81443
C	0.09947	2.73104	-0.27803
C	-0.37467	2.69418	1.89918
C	0	4.12063	0.14328
C	-0.33086	4.09537	1.5173
C	0.13134	5.33401	-0.55118
C	-0.53237	5.28169	2.24267
C	-0.0684	6.51927	0.17224
C	-0.39648	6.49373	1.5507
N	0.10842	-1.88078	0.81443
C	-0.09947	-2.73104	-0.27803

C	0.37467	-2.69418	1.89918
C	0	-4.12063	0.14328
C	0.33086	-4.09537	1.5173
C	-0.13134	-5.33401	-0.55118
C	0.53237	-5.28169	2.24267
C	0.0684	-6.51927	0.17224
C	0.39648	-6.49373	1.5507
N	0	0	2.72231
C	-0.41066	1.05365	3.50695
C	0.41066	-1.05365	3.50695
N	0.25104	2.38187	-1.54562
N	-0.60002	2.30696	3.16118
N	-0.25104	-2.38187	-1.54562
N	0.60002	-2.30696	3.16118
H	0.41171	2.49669	-4.49334
H	-0.41171	-2.49669	-4.49334
H	0.38273	5.3497	-1.61636
H	-0.78936	5.25589	3.30625
H	-0.38273	-5.3497	-1.61636
H	0.78936	-5.25589	3.30625
H	0.20368	1.22683	-6.65335
H	-0.20368	-1.22683	-6.65335
H	0.03027	7.48455	-0.33597
H	-0.54825	7.43932	2.0822
H	-0.03027	-7.48455	-0.33597
H	0.54825	-7.43932	2.0822
Ni	0	0	0.82121
H	-0.56593	0.82489	4.56977
H	0.56593	-0.82489	4.56977

Three lowest frequencies for optimized structure of nickel seco-porphyrazine **4** at PCM BP86/6-31G(d) level.

	1	2	3
	B	A	B
Frequencies --	20.5551	40.7631	53.5688
Red. masses --	6.3099	5.8566	6.0210
Frc consts --	0.0016	0.0057	0.0102
IR Inten --	0.0634	0.0057	1.4907

Supporting Information Table 1. Oscillator strengths, energies, and expansion coefficients calculated using PCM-TDDFT BP86/6-31G(d) level for *seco*-porphyrazine **4**.

Order	Symm	f	Energy_eV	Energy_nm	Energy_cm-1	Transition	Coef
1	Singlet-A	0.0023	1.5732	788.08	12689.1		
						127->129	0.67724
						127->130	-0.19344
2	Singlet-B	0.3831	1.7863	694.1	14407.1		
						126->128	0.20979
						127->128	0.6632
						127<-128	-0.10593
3	Singlet-B	0.04	1.8648	664.86	15040.8		
						125->128	0.15347
						126->128	0.65813
						127->128	-0.17846
4	Singlet-B	0.0232	1.9149	647.47	15444.7		
						125->128	0.68083
						126->128	-0.1202
						127->128	0.11781
5	Singlet-A	0.0005	2.076	597.23	16744		
						124->128	0.54947
						125->129	-0.1839
						126->129	-0.21612
						126->130	-0.33244
6	Singlet-A	0.2158	2.1111	587.31	17026.8		
						127->129	0.18486
						127->130	0.65681
7	Singlet-A	0.002	2.2702	546.14	18310.3		
						125->129	0.30956
						125->130	0.56171
						126->129	-0.25748
						126->130	0.13345
8	Singlet-A	0.0034	2.3779	521.4	19179.1		
						123->128	-0.30377
						124->128	0.1711
						125->130	0.23178
						126->129	0.54617
9	Singlet-B	0.036	2.3901	518.74	19277.5		
						124->129	0.45131
						124->130	0.52351
10	Singlet-B	0.009	2.5493	486.35	20561.3		
						119->129	-0.11152
						123->130	0.1175

						124->129	0.51239
						124->130	-0.44478
11	Singlet-A	0.0017	2.5941	477.95	20922.7		
						123->128	0.62558
						125->130	0.10474
						126->129	0.26253
						126->130	-0.12179
12	Singlet-A	0.0074	2.615	474.13	21091.3		
						119->128	-0.11665
						121->128	-0.12124
						122->128	0.14314
						124->128	0.34853
						125->130	-0.15128
						126->130	0.51553
13	Singlet-B	0.0007	2.7829	445.52	22445.7		
						123->129	0.70506
14	Singlet-A	0.0001	2.8548	434.3	23025.6		
						121->128	-0.11657
						125->129	0.57333
						125->130	-0.27823
						126->130	-0.23197
15	Singlet-A	0.0115	2.9268	423.61	23606.6		
						117->128	-0.13057
						121->128	-0.15466
						122->128	0.632
						124->128	-0.10319
						127->132	0.13513
16	Singlet-B	0.0482	2.9371	422.13	23689.4		
						120->128	0.66491
						127->131	-0.19056
17	Singlet-B	0.0041	2.9669	417.89	23929.7		
						123->130	0.67931
18	Singlet-A	0.0606	3.0052	412.56	24238.9		
						117->128	-0.18038
						121->128	0.60967
						122->128	0.1681
						127->132	-0.16461
19	Singlet-B	0.0049	3.0407	407.75	24524.8		
						118->128	0.17099
						120->128	0.17243
						121->129	0.10627
						121->130	0.12177
						127->131	0.62025

20	Singlet-B	0.012	3.0657	404.43	24726.2		
						122->129	0.68555
21	Singlet-B	0.001	3.1296	396.17	25241.7		
						119->129	-0.10906
						121->129	0.66932
						121->130	-0.12944
22	Singlet-A	0.0014	3.1392	394.96	25319		
						120->129	0.69174
23	Singlet-A	0.0201	3.238	382.9	26116.5		
						117->128	-0.12124
						119->128	0.46642
						120->130	-0.23026
						121->128	0.10351
						125->129	0.11003
						127->132	0.38391
24	Singlet-B	0.0183	3.2472	381.82	26190.4		
						116->128	0.21283
						118->128	0.51393
						121->130	-0.10715
						122->130	-0.35731
						126->131	-0.11031
						127->131	-0.11717
25	Singlet-B	0.0097	3.2612	380.18	26303.3		
						116->128	0.12486
						118->128	0.22593
						121->130	-0.13187
						122->130	0.47778
						126->131	0.16781
						127->133	0.38424
26	Singlet-A	0.0025	3.2757	378.5	26420.1		
						118->130	-0.12649
						119->128	0.4296
						120->130	0.17917
						121->128	-0.11578
						127->132	-0.42601
						127->134	0.17247
27	Singlet-B	0.002	3.3027	375.4	26638.3		
						114->128	-0.19254
						116->128	0.61913
						118->128	-0.12308
						127->133	-0.2027
28	Singlet-B	0.0261	3.3238	373.01	26808.9		
						116->128	0.13066

						118->128	-0.31485
						122->130	-0.24362
						126->131	-0.18523
						127->133	0.50869
29	Singlet-A	0.028	3.3386	371.36	26928		
						115->128	0.53285
						117->128	0.37076
						120->130	0.15171
30	Singlet-A	0.0697	3.3563	369.41	27070.2		
						113->128	0.12279
						115->128	0.4377
						117->128	-0.39526
						118->129	-0.1195
						119->128	-0.14772
						120->130	-0.14181
						127->134	-0.13594
31	Singlet-B	0.0015	3.3759	367.26	27228.7		
						114->128	-0.21781
						118->128	0.12026
						119->129	-0.17723
						119->130	-0.16158
						121->130	0.56938
						127->131	-0.12891
32	Singlet-A	0.0149	3.4327	361.19	27686.3		
						117->128	-0.18639
						120->129	0.10914
						120->130	0.57087
						124->133	0.10796
						127->132	0.22034
						127->134	-0.11365
33	Singlet-B	0.0006	3.4369	360.74	27720.8		
						114->128	-0.32691
						117->129	0.33221
						119->129	0.48442
						127->133	0.10433
34	Singlet-B	0.0136	3.4535	359.01	27854.4		
						114->128	0.40845
						115->129	0.10181
						116->128	0.10785
						117->129	-0.2517
						117->130	-0.13149
						119->129	0.35145
						121->130	0.21286

						126->131	0.13171
35	Singlet-B	0.0049	3.4756	356.72	28033.2		
						114->128	0.29756
						117->129	0.48298
						117->130	-0.11842
						119->129	-0.15918
						125->131	0.29053
						126->131	0.10927
36	Singlet-A	0.0108	3.4904	355.22	28151.6		
						114->129	-0.25821
						116->129	-0.32228
						117->128	-0.1549
						118->129	0.50642
						127->134	0.16909
37	Singlet-B	0.0272	3.4931	354.94	28173.8		
						114->128	-0.13043
						117->129	-0.24582
						119->130	0.11142
						125->131	0.58486
						126->131	0.19289
38	Singlet-B	0.2533	3.5098	353.25	28308.6		
						115->129	-0.12346
						119->129	-0.1222
						119->130	0.17592
						122->130	-0.21323
						125->131	-0.26544
						126->131	0.53097
						126->133	-0.10762
39	Singlet-A	0.0014	3.5146	352.77	28347.1		
						116->129	0.39198
						116->130	-0.10218
						118->130	0.20352
						124->131	-0.1037
						126->132	-0.14304
						127->132	0.11445
						127->134	0.4721
40	Singlet-A	0.0081	3.5464	349.61	28603.3		
						113->128	-0.16807
						114->129	-0.13612
						116->129	0.45412
						118->129	0.34302
						118->130	-0.15434
						127->134	-0.26797

41	Singlet-B	0.0306	3.5732	346.99	28819.3		
						115->129	0.35125
						119->130	0.55344
						124->132	-0.13762
						126->131	-0.10035
42	Singlet-B	0.0592	3.5763	346.69	28844.2		
						115->129	0.55163
						117->130	0.26444
						119->130	-0.26371
						124->132	0.13864
						126->131	0.12676
43	Singlet-A	0.0532	3.5781	346.51	28859.2		
						124->131	0.65565
						124->133	0.12004
						126->132	-0.11865
						127->134	0.13162
44	Singlet-A	0.0167	3.645	340.15	29398.8		
						114->129	0.5217
						114->130	-0.10767
						116->130	-0.18197
						118->129	0.19767
						125->132	-0.31287
45	Singlet-A	0.0289	3.65	339.68	29439.5		
						114->129	0.13735
						116->130	-0.14303
						118->130	-0.18263
						125->132	0.16527
						126->132	0.55184
						126->134	0.13518
						127->134	0.16438
46	Singlet-A	0.0094	3.6635	338.43	29548.2		
						114->129	0.17496
						118->129	0.12146
						118->130	0.24985
						125->132	0.58568
						126->132	-0.10237
						127->134	-0.11059
47	Singlet-A	0	3.7146	333.78	29959.9		
						113->128	0.17496
						114->129	0.14893
						114->130	-0.20756
						116->130	0.60632
48	Singlet-B	0.0388	3.7231	333.01	30029.1		

						115->130	0.10362
						117->130	0.12908
						126->133	0.65602
49	Singlet-B	0.0436	3.7412	331.4	30175		
						115->130	0.38346
						117->130	-0.11862
						124->132	0.54418
50	Singlet-B	0.0214	3.7607	329.68	30332.4		
						115->130	0.5745
						124->132	-0.35202