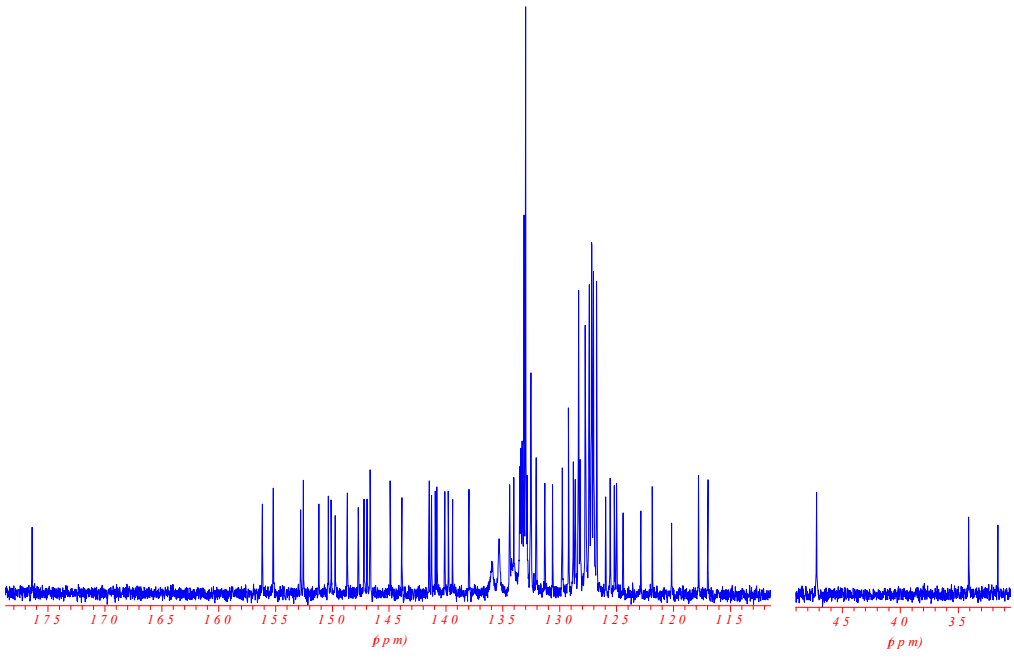
S1

NMR data for 2-(21'-(5',10',15',20'-tetraphenyl-2'-aza-21'-carbaporphyrinatonic-kel(II)))-methyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrinatonickel(II) **5**

δ_H($CDCl_3$, 298 K) 9.35 (s, 1H, 3'), 8.57 (d, 5.0 Hz, 1H, p'), 8.53 (d, 5.0 Hz, 1H, p'), 8.48 (d, 4.6 Hz, 1H, p'), 8.46 (d, 4.6 Hz, 1H, p'), 8.44 (d, 5.0 Hz, 1H, p'), 8.38 (d, 5.0, 1H, p'), 8.21 (b, 1H), 8.20 (d, 4.0 Hz, 1H,p), 8.20 (b, 1H), 8.14 (b, 2H), 8.01 (m, 2H), 7.94 (m, 1H), 7.88 (d, 5.0 Hz, 1H, p), 7.85 (d, 5.0 Hz, 1H, p), 7.82 (b, 2H), 7.80 (d, 5.0 Hz, 1H, p), 7.78 (b, 4H), 7.66 (b, 1H), 7.61-7.50 (overlapping multiplets, 7H), 7.41 (m, 2H), 7.34 (d, 5.0 Hz, 1H, p), 6.96 (d, 5.0 Hz, 1H, p), 6.71 (s, 1H, 3), 5.79 (m, 1H, *ortho*, 20-Ph), 5.57 (overlapping multiplets, 2H, *ortho*+*para*, 20-Ph), 5.47 (m, 1H, *meta*, 20-Ph), 5.40 (m, 1H, *meta*, 20-Ph), 0.11 (d, 15.6 Hz, 1H, 2,21'-CH_2), –0.47 (d, 15.6 Hz, 1H, 2,21'-CH_2);

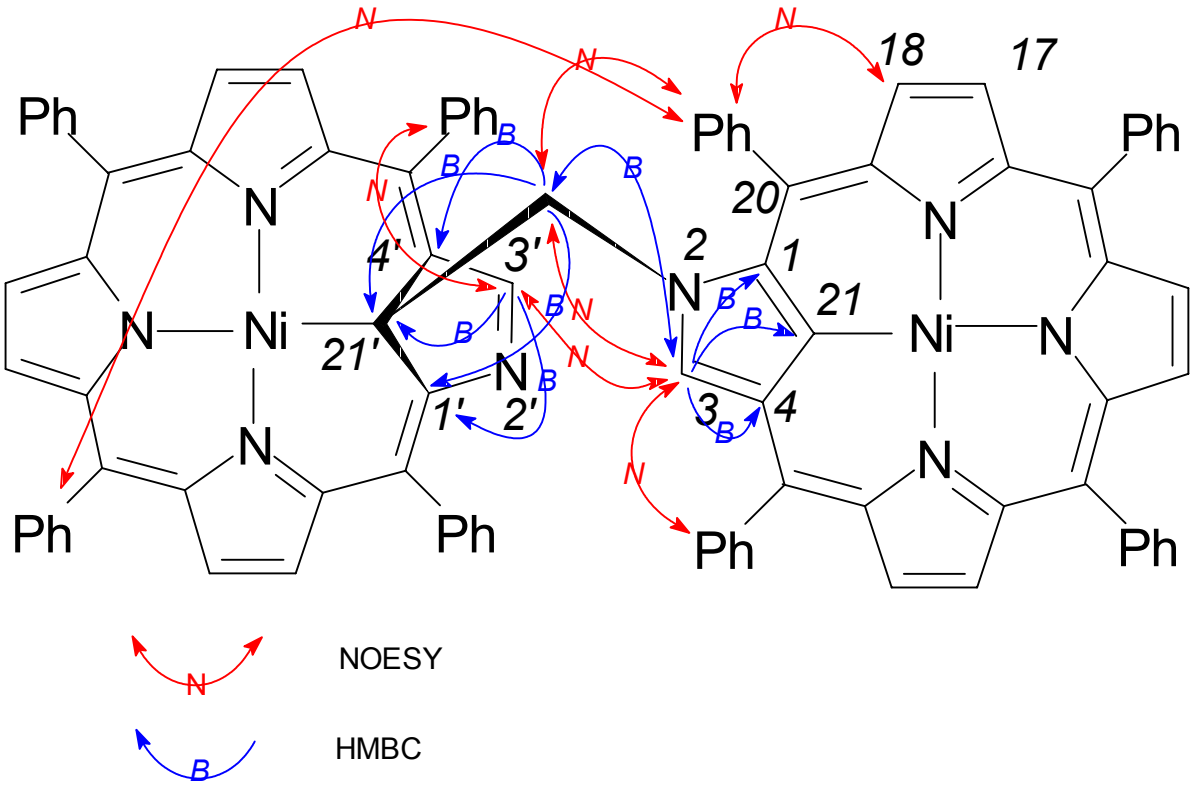
δ_C($CDCl_3$, 298 K) 176.4 (1'-*C*), 156.1, 155.2 (3'-*C*H) 152.8, 152.5, 151.2 (4'-*C*), 150.3, 150.1, 149.7, 148.7,147.7, 147.2, 146.9, 146.7 (3-*C*H), 144.9, 143.9, 141.5, 141.3, 140.9, 140.8, 140.1, 139.8, 139.4, 137.9, 136.0, 135.3, 134.4 (1-*C*), 134.2, 134.0, 133.5, 133.4, 133.3, 133.1, 133.0, 133.0, 132.8, 132.6, 132.5, 132.0, 131.3, 130.6, 129.8, 129.2, 128.8, 128.6, 128.3, 128.3, 128.2, 127.7, 127.4, 127.2, 127.2, 127.0, 126.9, 126.7, 125.9, (4-*C*) 125.5, 125.2 125.0, 124.4, 122.8, 121.8 (21-*C*), 120.1, 117.8, 116.9, 47.2 (2,21'-*C*H_2), 34.1 (21'-*C*)

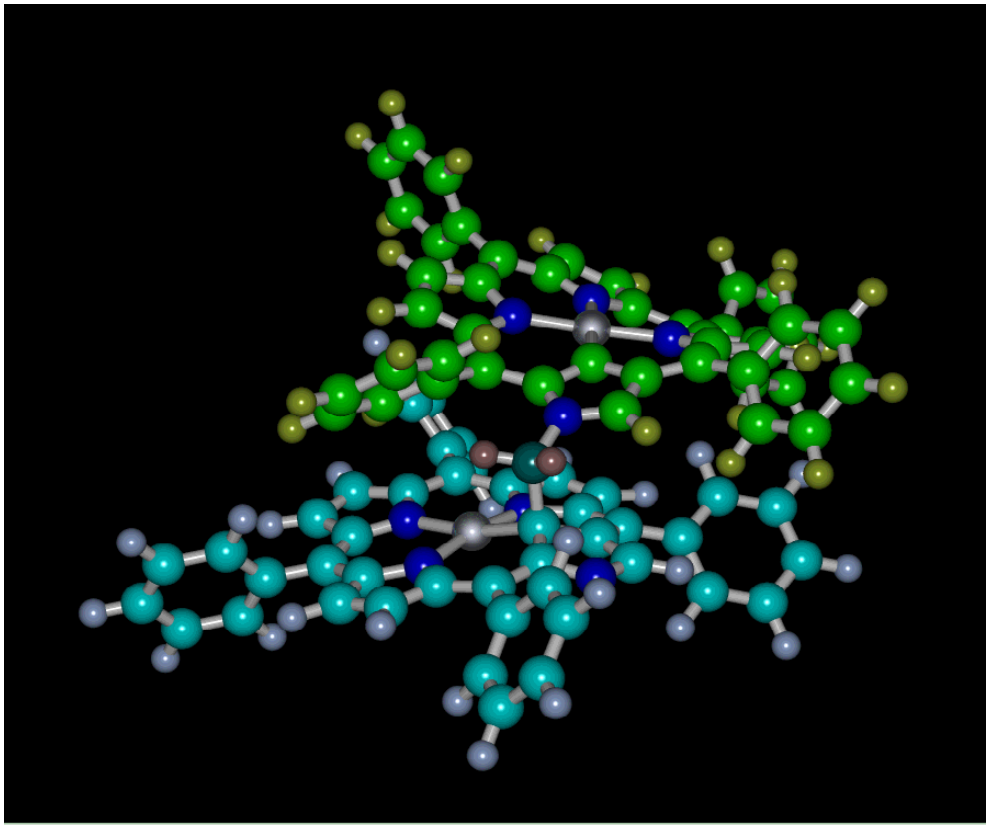


125.7 MHz ^{13}C NMR spectrum of **5**, $CDCl_3$, 298K

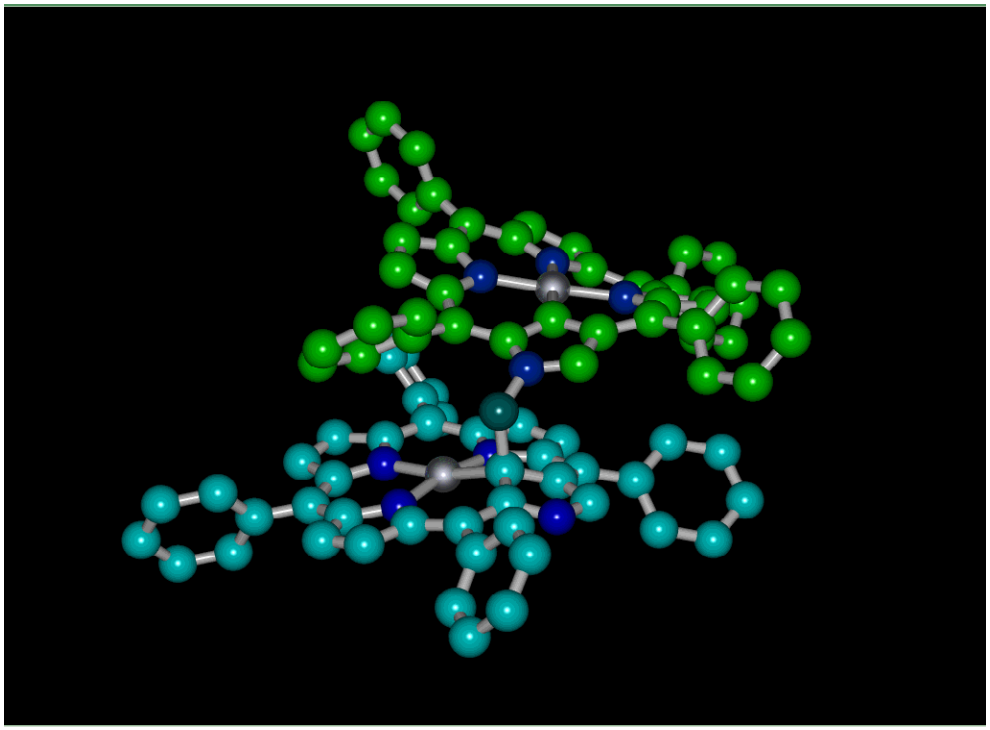
S2

Important trough-space proton-proton contacts (NOESY) and long-range proton-carbon couplings (HMBC) observed for 2-(21'-(5',10',15',20'-tetraphenyl-2'-aza-21'-carbaporphyrinatonickel(II)))-methyl-5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrinatonickel(II) **5**





Molecular model of **5** optimized by MM+ forcefield based on NMR data.



Molecular model of **5** optimized by MM+ forcefield based on NMR data. Protons are omitted for clarity.

S4

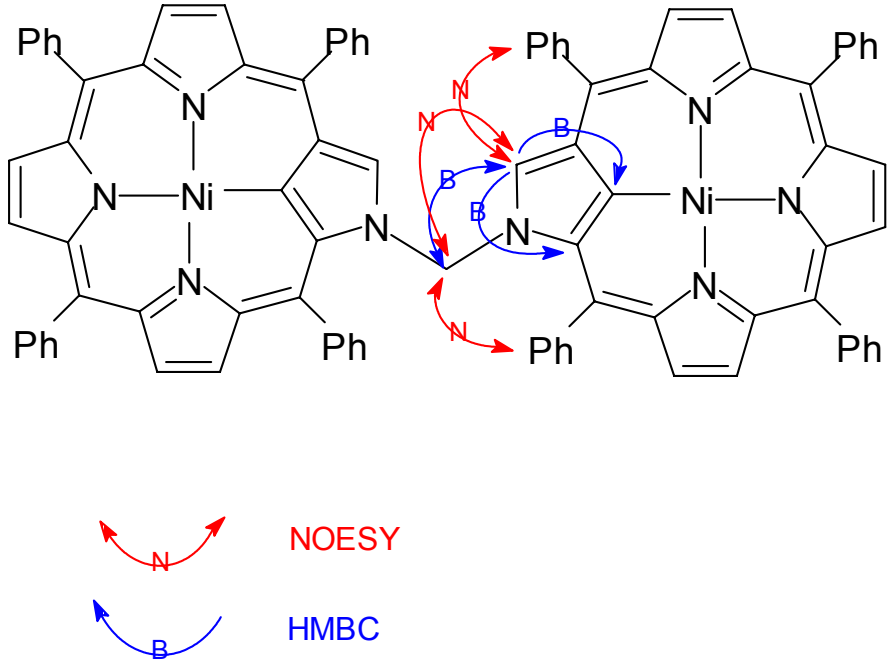
NMR data for bis-(2,2'-(5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrinatonickel(II))methane **6**

δ_H(500 MHz, $CDCl_3$, 298 K) 7.86 (2H, d, 4.9 Hz), 7.81 (2H, d, 4.9 Hz), 7.79 (2H, d, 4.7 Hz), 7.79 (b,4H), 7.78 (2H, s, 3), 7.76 (4H, b), 7.64 (2H, d, 4.7 Hz), 7.61 (2H, d, 4.7 Hz), 7.54 (6H, m), 7.52 (2H, d, 4.9 Hz),, 7.48 (2H, d, 7.2 Hz), 7.41 (2H, b), 7.39 (2H, d, 7.8 Hz), 7.26 (4H, b), 7.14 (2H, d, 7.5 Hz), 6.95 (4H, m), 6.86 (4H, b), 5.55 (2H, s, -CH_2-).

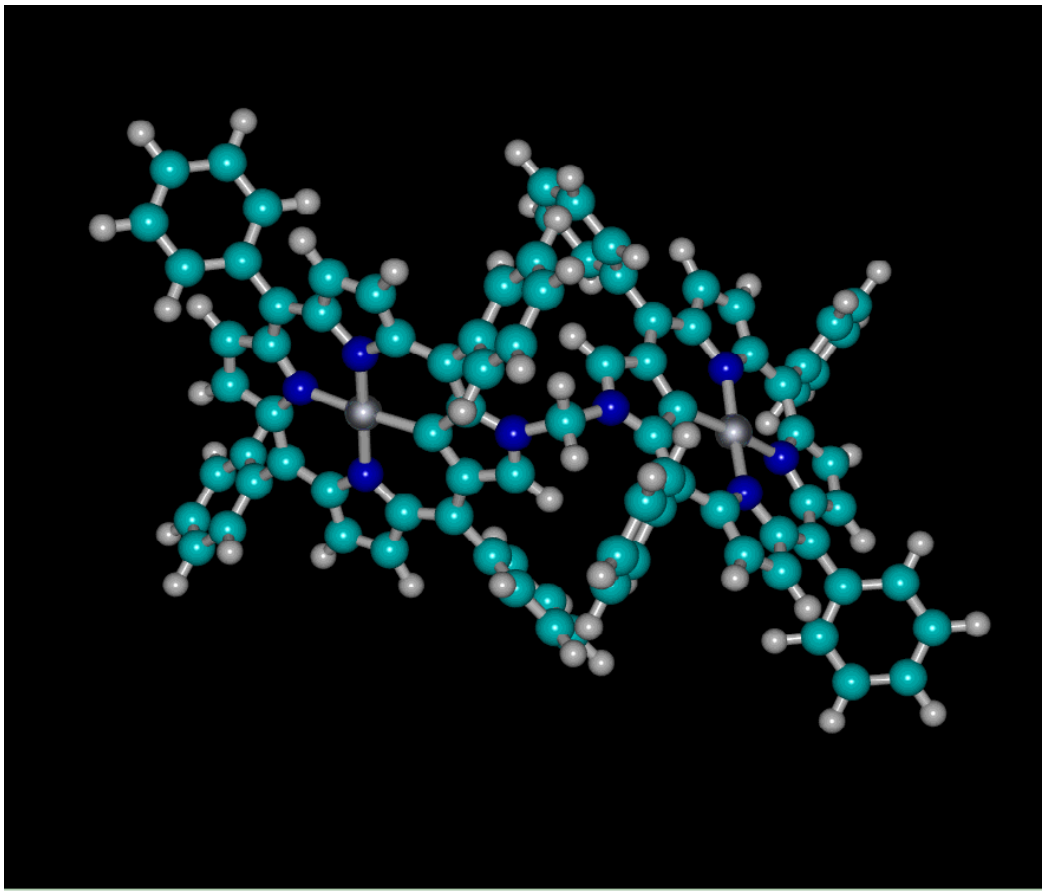
δ_H(500 MHz, $CDCl_3$, 213 K) 7.94 (2H, s, 3), 7.91 (2H, d, 5.2 Hz), 7.87 (2H, d, 4.8 Hz), 7.84 (2H, d, 5.2 Hz), 7.79 (4H, m), 7.75 (2H, d, 7.0 Hz), 7.72 (2H, d, 6.4 Hz), 7.69 (2H, d, 5.2 Hz), 7.65 (2H, b), 7.62 (2H, d, 5.2 Hz), 7.60 (2H, d, 5.2 Hz),, 7.56 (8H, overlapping multiplets), 7.50 (2H, d, 7.3 Hz), 7.42 (2H, d, 7.4 Hz), 7.39 (2H, d, 6.7 Hz), 7.32 (2H, t, 7.4 Hz), 7.21 (4H, t, 6.6 Hz), 7.15 (2H, d, 7.4 Hz), 7.04 (4H, overlapping multiplets), 6.79 (2H, t, 7.4 Hz), 6.69 (2H, t, 7.4 Hz), 5.55 (2H, s, -CH_2-).

δ_C(125.7 MHz, $CDCl_3$, 298 K) 154.6, 154.5, 152.3, 151.6, 149.7, 149.0, 148.8 (3-*C*H), 146.1, 146.0, 145.4, 145.2, 141.2, 140.8, 134.1 (1-*C*), 133.9, 133.2, 133.1, 133.0, 132.5, 132.2, 131.7, 131.7, 131.3, 130.3, 128.3, 127.9, 127.4, 127.3, 127.1, 123.0 (21-*C*), 64.6 (–*C*H_2–).

Important trough-space proton-proton contacts (NOESY) and long-range proton-carbon couplings (HMBC) observed for bis-(2,2'-(5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrinatonickel(II))methane **6**



S6



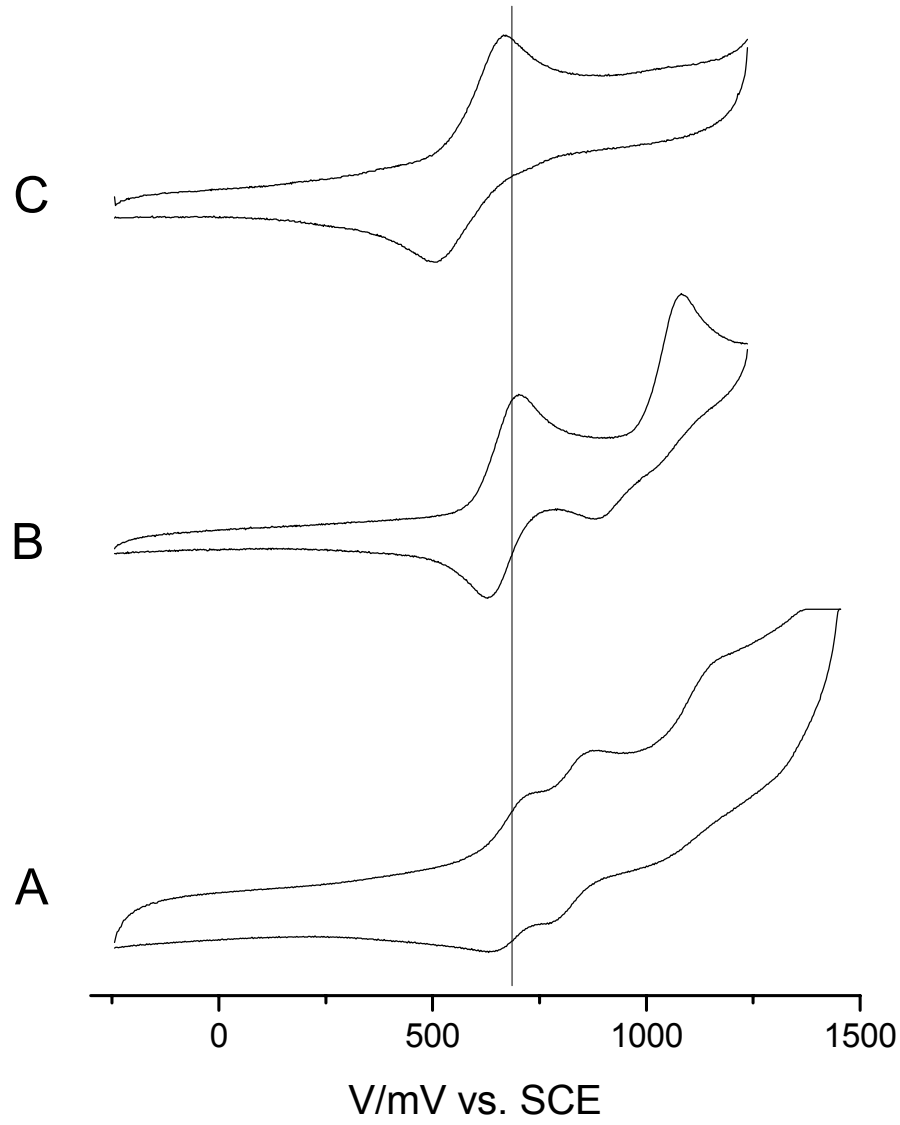
Molecular model of **6** optimized by MM+ forcefield based on NMR data.

^{1}H NMR data for **5**-HCl, 298 K, $CDCl_3$

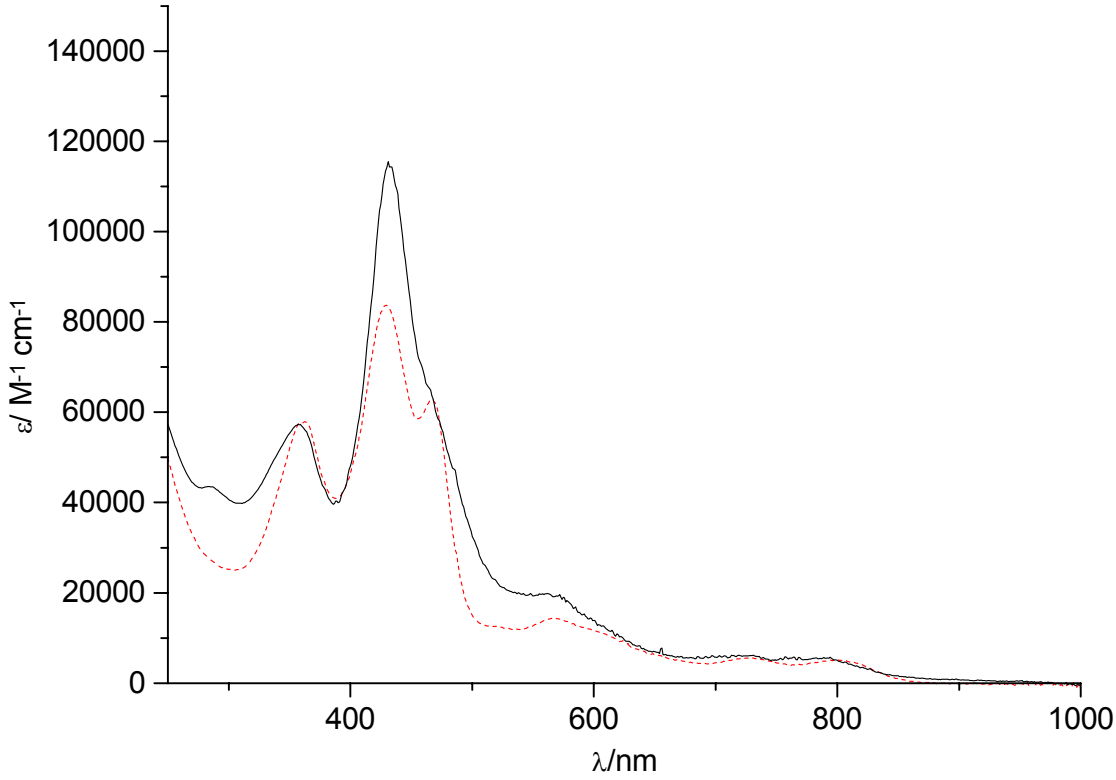
59.9 (CH_2), 56.3 (p'), 55.2 (p'), 52.3 (p'), 48.3 (p'), 43.1 (CH_2), 22.7 (p'), 20.9 (3), 20.3 (p'), 11.4, 10.7, 10.3, 10.0, 9.5, 9.3, 9.2, 9.0, 8.6, 8.3, 8.1, 7.9, 6.8, 6.5, 6.3, 0.3, -1.6, -2.3 (3'), -3.3, -22.8 (2'-NH)

^{1}H NMR data for **5**-HCl, 213 K, $CDCl_3$

78.9 (CH_2), 73.8 (p'), 72.5 (p'), 68.4 (p'), 63.1 (p'), 59.8 (CH_2), 28.9 (p'), 25.9 (p'), 25.7 (3), 12.9, 12.3,12.0, 11.2, 10.2, 10.0, 9.8, 9.0, 9.0, 8.9, 8.4, 8.2, 8.1, 7.8, 7.6, 7.6, 7.0, 6.4, 6.0, 5.9, -1.9, -2.0, -4.4, -4.8, -6.3, -7.8 (3'), -35.5 (2'-NH)



Cyclic voltammograms of **5** (trace A), **3** (trace B), and **4** (trace C) in CH_2Cl_2 (supporting electrolyte: 0.1 M tetrabutylammonium perchlorate; working electrode: glassy carbon; reference electrode: SCE).



Electronic spectra of **5** (solid line) and **6** (dashed line), CH_2Cl_2, 298K.