Electronic Supplementary Information

of the manuscript:

Single Azopyridine-Substituted Porphyrin Molecules For Configurational and Electronic Switching†

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Synthesis of the azopyridine-functionalized Ni-tetraphenylporphyrin (1). As a precursor for the preparation of azopyridine-functionalized porphyrin **1**, dipyrromethane **2** was synthesized by the condensation of pyrrole and benzaldehyde (3:1 mole ratio) in a 0.18 M HCl solution at room temperature. Flash chromatography on silica gel, with cyclohexane/CH_2Cl_2/triethylamine (48/50/2) as the eluent and subsequent crystallization yielded 40 % of the dipyrromethane **2**. The use of a mildly basic medium prevented the decomposition of the dipyrromethane on the silica column. A high purity of the dipyrromethane is essential for the synthesis of *meso*-substituted porphyrin **1**.

The 3-phenylazopyridine functionalized benzaldehyde **4** was synthesized using a standard Suzuki-Miyaura cross-coupling reaction between azopyridine **3** and 2-formylphenylboronic acid in 95% yield in the presence of catalytic amounts of $Pd(PPh_3)_4$. The synthesis of azopyridine **3** was performed by a conventional two step method, which involved the reduction of 3-bromonitrobenzene to the nitroso derivative followed by condensation with 3-aminopyridine. The reduction of 3-bromonitrobenzene was performed under weak acidic conditions using Zn powder in the presence of NH_4Cl at room temperature followed by treatment with aqueous $FeCl_3$ solution at 0 °C. The solid nitrosobenzene derivative was coupled directly with 3-aminopyridine in a biphasic mixture of toluene and 40% NaOH solution under heating to obtain azopyridine **3** in 35% yield. The porphyrin with the azopyridine side arm was synthesized via a mixed condensation of dipyrromethane **2**, aldehyde **4** and benzaldehyde in CH_2Cl_2 in the presence of catalytic amounts of $BF_3{\cdot}OEt_2$, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).

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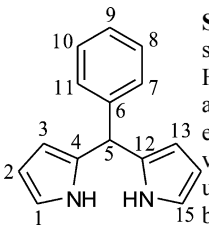
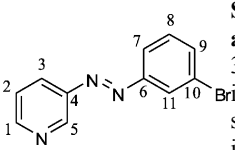
The porphyrins were separated by flash chromatography using dichloromethane/ethyl acetate as eluents. The first purple band that was eluted with CH_2Cl_2 was identified as the *meso*-tetraphenylporphyrin and the second purple band was isolated (95% CH_2Cl_2/5% EtOAc) as the desired porphyrin in 6.65% yield. Finally, the target Ni-porphyrin **1** was synthesized in 84% yield from the corresponding porphyrin using $Ni(acac)_2$ in toluene under reflux for 3h. The structure of Ni-porphyrin **1** was unambiguously elucidated by UV, mass spectroscopy, 1-D and 2D-NMR spectroscopy and elemental analysis.

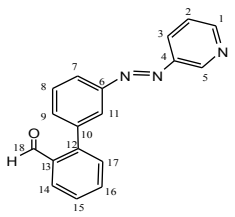


Synthesis of dipyrromethane 2.[i, ii, iii] To a solution of 400 mL of 0.18 M aqueous HCl pyrrole (8.05 g, 120 mmol, 3 equiv.) and benzaldehyde (4.24 g, 40 mmol, 1 equiv.) were added. The mixture was vigorously stirred at room temperature under nitrogen atmosphere. The solution became white and slowly a precipitated was formed which often sticked to the flask (disturbed the stirring) and the solid product slowly turned brown. The mixture was stirred for 2.5 h and the water was removed by decantation. The solid product was dissolved in CH_2Cl_2 (150 mL) and the organic layer was washed by $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated under reduced pressure. Flash chromatography over silica gel using cyclohexane/CH_2Cl_2/triethylamine (48/50/2) as the eluent and subsequent crystallization from cyclohexane/CH_2Cl_2 yielded the dipyrromethane **2** (3.59 g, 16.15 mmol, 40%) as a white crystalline compound, mp: 103 °C. IR (cm^{-1}): 3335, 1552, 1454, 1112, 1023; ^1H NMR ($CDCl_3$, 500 MHz): δ = 5.45 (s, 1H, H-5), 5.90-5.92 (m, 2H, H-3 & 13), 6.15 (ddd, *J* = 4.25, 4.25, 2.5 Hz, 2H, H-2 & 14), 6.67-6.68 (m, 2H, H-1 & 15), 7.17 -7.22 (m, 2H, H-7 & 11), 7.23-7.26 (m, 1H, H-9), 7.29-7.33 (m, 2H, H-8 & 10); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 44.01 (C-5), 107.26 (C-3 & 13), 108.47 (C-2 & 14), 117.24 (C-1 & 15), 127.02 (C-9), 128.43 (C-7 & 11), 128.68 (C-8), 132.51 (C-4 & 12), 142.09 (C-6) ppm; MS [m/z (%)] 222.1 (100), 221.1 (38), 145.1 (61).

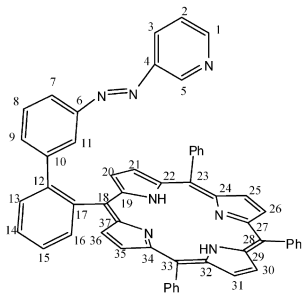


Synthesis of (3-Bromophenyl)-3-azopyridine 3. To a stirred solution of 3-bromonitrobenzene (8.08 g, 40 mmol) in ethanol (150 mL) was added a solution of NH_4Cl (3.21 g, 60 mmol) in 15 mL of H_2O under nitrogen

atmosphere. The resulting mixture was heated to 40 ºC until a clear solution was obtained. To this solution Zn powder (6.54 g, 100 mmol) was added slowly at room temperature over a period of 20 min. After stirring for 2 h the resulting reaction mixture was filtered, and washed with ethanol and water successively. The light yellow combined filtrate was then added drop wise into an ice-cold solution of $FeCl_3.6H_2O$ (18 g) in H_2O (200 mL) with vigorous stirring. A light yellow precipitate was formed which was collected by suction filtration and washed with water. The product was air dried for two days and the crude product (7.2 g, 38.70 mmol) was slowly added to a stirred biphasic solution of 3-aminopyridine (3.57 g, 38 mmol) in toluene (30 mL) and 40% NaOH solution (20 mL) at 80^0C under nitrogen atmosphere. The mixture was heated to reflux for 2.5 h. Then the reaction mixture was allowed to attain room temperature and was extracted with ethyl acetate (150 mL). The ethyl acetate extract was washed with water (2 x 100 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel using ethyl acetate and cyclohexane (3:7) as the eluent to obtain a pure orange red solid **3** (3.47 g, 13.24 mmol, 35 %), R_f = 0.53 (1:1 ethyl acetate and cyclohexane), mp: 71.5 ºC. IR(cm^{-1}): 3057, 1570, 1449, 1422, 812, 780, 696, 674; UV-vis ($CHCl_3$) λmax (nm): 319 (0.66), 242 (0.41); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.42 (t, *J* = 8.0 Hz, 1H, H-8), 7.45 (ddd, *J* = 8.0, 4.7, 0.7 Hz, 1H, H-2), 7.63 (ddd, *J* = 7.9, 1.95, 1.0 Hz, H-7), 7.91 (ddd, *J* = 8.0, 1.85, 1.0 Hz, H-9), 8.08 (t, *J* = 1.85 Hz, 1H, H-11), 8.13 (ddd, *J* = 8.20, 2.34, 1.6 Hz, 1H, H-3), 8.72 (dd, *J* = 4.72, 1.6 Hz, 1H, H-1), 9.20 (dd, *J* = 2.4, 0.5 Hz, 1H, H-5); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 123.14 (C-9), 123.24 (C- 10), 124.03 (C-2), 124.87 (C-11), 126.97 (C-3), 130.57 (C-8), 134.35 (C-7), 147.55 (C-4), 147.61 (C-5), 152.24 (C-1), 153.31 (C-6) ppm; MS [m/z (%)] 262.0 (100), 261.0 (49), 260.0 (97), 259.0 (32); Elemental analysis: Calcd. For $C_{11}H_8BrN_3$: C 50.41; H 3.08; N 16.03; found: C 50.50; H 3.07; N 16.01.

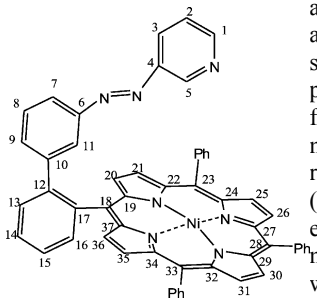


Synthesis of 2-(3-phenylazopyridine)-benzaldehyde 4: To a stirred solution of **3** (1.00 g, 3.81 mmol) in dry toluene (30 mL) under nitrogen atmosphere were successively added 2-formylphenylboronic acid (630 mg, 4.2 mmol), ethanol (10 mL), K_2CO_3 (2 mL, 2 M solution in water) and $Pd(PPh_3)_4$ (60 mg). Then the resulting biphasic mixture was stirred vigorously and heated to 90 ºC. The progress of the reaction was followed by TLC. After heating for 16 h (oil bath) the mixture was cooled down to room temperature and extracted with ethyl acetate (100 mL). The organic layer was separated and washed with water (2 x 50 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The dark orange residue was purified by flash column chromatography on silica gel by using ethyl acetate and hexane (3:7) as the eluent to afford the compound **4** as an orange red solid (1.04 g, 3.61 mmol, 95%), R_f = 0.44 (40% ethyl acetate and cyclohexane), mp 97.2 ºC. IR (cm^{-1}): 3045, 2862, 1685, 1589, 1190, 815, 758, 678; UV-vis ($CHCl_3$) λ max (nm): 320 (0.83), 257 (0.62), 242 (0.67); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.47 (dd, *J* = 8.0, 4.7 Hz, 1H, H-2), 7.52-7.58 (m, 3H, H-9, H-15 and H-17), 7.66 (t, *J* = 8.0 Hz, 1H, H-8), 7.69 (td, *J* = 7.50, 1.4 Hz, 1H, H-16), 7.98 (t, *J* = 2.0 Hz, 1H, H-11), 8.04 (dt, *J* = 8.0, 1.6 Hz, 1H, H-7), 8.07 (dd, *J* = 8.0, 1.5 Hz, 1H, H-14), 8.17 (dt, *J* = 8.0, 2.0 Hz, 1H, H-3), 8.73 (dd, *J* = 5.0, 1.5 Hz, 1H, H-1), 9.22 (d, *J* = 2.30 Hz, 1H, C-5), 10.06 (d, *J* = 0.6 Hz, 1H, H-18); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 123.09 (C-7), 124.04 (C-2), 124.07 (C-11), 127.01 (C-3), 127.95 (C-14), 128.31 (C-9), 129.31 (C-8), 130.82 (C-15), 133.10 (C-17), 133.73 (C-13), 133.78 (C-16), 139.02 (C-10), 144.80 (C-12), 147.46 (C-5), 157.74 (C-4), 152.00 (C-1), 152.33 (C-6), 191.45 (C-18) ppm; MS [m/z (%)] 277.1 (75), 278.1 (42), 287.1 (100). Elemental analysis: Calcd. For $C_{18}H_{13}N_3O$: C 75.25; H 4.56; N 14.63; found: C 75.24; H 4.75; N 14.79.



Synthesis of the azopyridine functionalized porphyrin. In a 500 mL two neck round-bottom flask CH_2Cl_2 (300 mL), dipyrromethane **2** (777 mg, 3.5 mmol), aldehyde **4** (500 mg, 1.74 mmol) and benzaldehyde (180 mg, 1.70 mmol) were added successively, and the flask was wrapped in aluminum foil. The mixture was vigorously stirred and purged with nitrogen for 15 min at room temperature, and then $BF_3{\cdot}OEt_2$ (3.15 mmol, 1.5 mL of 2.5 M stock solution in CH_2Cl_2) was added via a syringe. The reaction mixture was stirred for 14 h at room temperature. Then DDQ (500 mg, 2.20 mmol) was added and the mixture was stirred for an additional 12 h. To this mixture Et_3N (0.5 mL, 3.60 mmol) was added and the solvent was evaporated to dryness under vacuum. The crude dark purple product was subjected to flash chromatography on silica gel using CH_2Cl_2 to separate tetraphenylporphyrin as the first fraction and then 5% ethyl acetate in CH_2Cl_2 was used as the eluent to collect the second purple fraction as the desired product. The second fraction was further purified by flash chromatography under similar conditions to obtain the pure monofunctionalized porphyrin (90 mg, 0.133 mmol, 6.65%). R_f = 0.66 (7% EtOAc and CH_2Cl_2). IR (cm^{-1}): 3295, 1676, 1467, 1438, 964, 796, 697; UV-vis ($CHCl_3$) λmax (nm): 552 (0.05), 517 (0.13), 421 (2.30), 320 (0.25); H NMR ($CDCl_3$, 500 MHz): δ = -2.8 (s, 2H, -NH), 6.42 (t, *J* = 8.0 Hz, 1H, C-8), 6.98 (d, *J* = 8.0 Hz, 1H, H-9), 7.06 (d, *J* = 8.0 Hz, 1H, H-7), 7.17 (dd, *J* = 8.1, 4.5 Hz, 1H, H-2), 7.51 (dd, *J* = 8.2 and 1.7 Hz, 1H, H-3), 7.69 (m, 1H, H-15), 7.69-7.75 (m, 9H, *m*-Ph-H + *p*-Ph-H), 7.87 (t, *J* = 1.8 Hz, 1H, H-11), 7.89 (m, 1H, H-14), 7.90 (m, 1H, H-13), 8.11-8.21 (m, 7H, H-16, *o*-Ph-H), 8.53 (dd, *J* = 4.8, 1.0, 1H, H-1), 8.75 (s, 1H, H-5), 8.77-8.83 (m, 8H, Pyrrole-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 118.41 (C-18), 120.06 (C-23, C-33), 120.28 (C-28), 121.26 (C-7), 123. 46 (C-11), 123.60 (C-2), 125.95 (C-15), 126.66 (C-3, 6C of *m*-Ph-CH), 127.70 (2C of *p*-Ph-CH), 128.06 (1C of *p*-Ph-CH), 128.80 (C-14), 129.50 (C-13), 131.12 (br, 8C of pyrrole-CH), 132.41 (C-9), 134.40 (2C of *o*-Ph-CH), 134.50 (2C of *o*-Ph-CH), 134.60 (2C of *o*-Ph-CH), 135.90 (C-16), 140.43 (C-17), 142.02 (2C, C_q of Phenyl), 142.13 (1C, C_q of Ph), 142.68 (C-10), 143.58 (C-12), 146.80 (C-5), 147.20 (C-4), 151.35 (C-1), 151.58 (C-6) ppm; MS [m/z] 795.2 (100), 796.2 (64%), 797.2 (20%); HRMS cacld. for $C_{55}H_{37}N_7$: 795.3110, found: 795.3094 (100%); Elemental analysis: Calcd. For $C_{55}H_{37}N_7$: C 83.00; H 4.69; N 12.32; found: C 82.186; H 4.93; N 12.06.

Synthesis of Ni-azopyridine functionalized porphyrin 1. To a stirred solution of porphyrin (Figure 7) (50 mg, 0.0628 mmol) in toluene (5 mL) $Ni(acac)_2$ (32 mg, 0.126 mmol) was



added under nitrogen atmosphere. The mixture was slowly refluxed and the progress of the reaction was followed by TLC. After 3 h the mixture was cooled down to room temperature and water (10 mL) was added and extracted by ethyl acetate (25 mL). The ethyl acetate extract was dried over Na_2SO_4 and purified by flash column chromatography on silica gel using 5 % ethyl acetate in CH_2Cl_2 to obtain a purple solid product **1** (Figure 8) (45 mg, 0.05278 mmol, 84%); R_f = 0.68 (7% EtOAc and CH_2Cl_2). IR (cm^{-1}): 2917, 1559, 1438, 1070, 1003, 794, 697; UV-vis ($CHCl_3$) λmax (nm): 530 (0.25), 451 (0.35), 417 (2.02), 327 (0.48); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.49 (t, *J* = 8.0 Hz, 1H, H-8), 6.80 (d, *J* = 8.0 Hz, 1H, H-9), 7.06 (d, *J* = 8.0 Hz, 1H, H-7), 7.14 (br, 1H, H-2), 7.36 (d, *J* = 8.0 Hz, 1H, H-3), 7.58 (m, 1H, H-11), 7.59-7.71 (m, 10H, H-15, *m*-Ph-H and *p*-Ph-H), 7.77-7.82 (m, 2H, H-13 and H-14), 7.90 (br, 6H, *o*-Ph-H), 8.18 (d, *J* = 7.0 Hz, 1H, H-16), 8.53 (br, 1H, H-1), 8.66-8.71 (m, 9H, H-5 and pyrrole-H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 117.61 (C-18), 119.00 (C-23 and C-33), 119.14 (C-28), 121.27 (C-7), 123.17 (C-11), 123.66 (C-2), 126.74 (C-3), 126.82 (6C for *m*-Ph-CH), 127.70 (3C for *p*-Ph-CH), 127.09 (C-8), 128.77 (C-14), 129.52 (C-13), 132.01 (2C for pyrrole-CH), 132.09 (2C for pyrrole-CH), 132.13 (2C for pyrrole-CH), 132.47 (C-9), 133.64 (2C for *o*-Ph-CH), 133.69 (4C for *o*-Ph-CH), 135.38 (C-16), 139.16 (C-17), 140.90 (3C for C_q of Ph), 142.31 (C-10), 142.62 (2C for Cq of pyrrole), 142.66 (2C for Cq of pyrrole), 142.78 (2C for Cq of pyrrole), 143.11 (C-12), 143.15 (2C for Cq of pyrrole), 146.55 (C-5), 147.41 (C-4), 151.30 (C-1), 151.58 (C-6) ppm; MS[m/z (%)] 851.2 (100), 852.2 (63), 853.2 (58), 854.2(27); HRMS cacld. for $C_{55}H_{35}N_7Ni$: 851.2307, found 851.2308 (100%). Elemental analysis: Calcd.(%) for $C_{55}H_{35}N_7Ni$: C 77.48; H 4.14; N 11.50; found: C 78.21 ; H 5.23; N 10.56.

Photochemistry. In order to investigate the switching behavior of the *trans*-azopyridine tethered Ni-porphyrin **1**, the compound was irradiated with UV light of various wavelengths (e. g. 365 nm and 310 nm) in $CDCl_3$ solution. ^{1}H NMR spectroscopy was used to analyze the photoreactions (Fig.SI1). *Cis-trans* isomerization with 365 nm UV light is very slow, and even after 1.5 h irradiation only little change was observed. However, after prolonged irradiation (12 h) at 365 nm new signals appeared (Fig.SI2). Similar changes were also observed upon irradiation with UV light of 310 nm after 4.5 h. It seems that the shorter wavelength is more efficient in inducing the switching process (15-20% conversion to cis). Most efficient is the irradiation into the Q band of the porphyrin at 520 nm (35-40% conversion to cis). However, the reverse process, *cis*- to *trans*- isomerization is very slow at room temperature, only a small amount of the *cis* isomer switched back to the *trans* configuration even after few days. Irradiation using visible light of different wavelengths was attempted (for example 440 nm) for reisomerization, however, no significant isomerization was observed. However, after heating at 70-75 °C for 2 h most of the *cis* isomer switched back to the *trans* configuration.

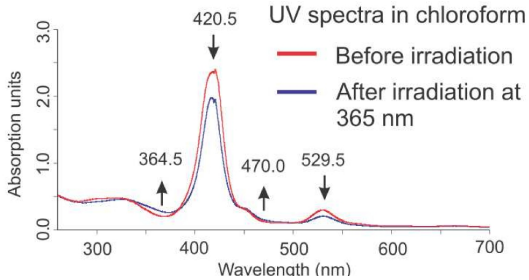


Figure SI2. UV spectra of **1** before and after one hour irradiation at 365 nm in chloroform.

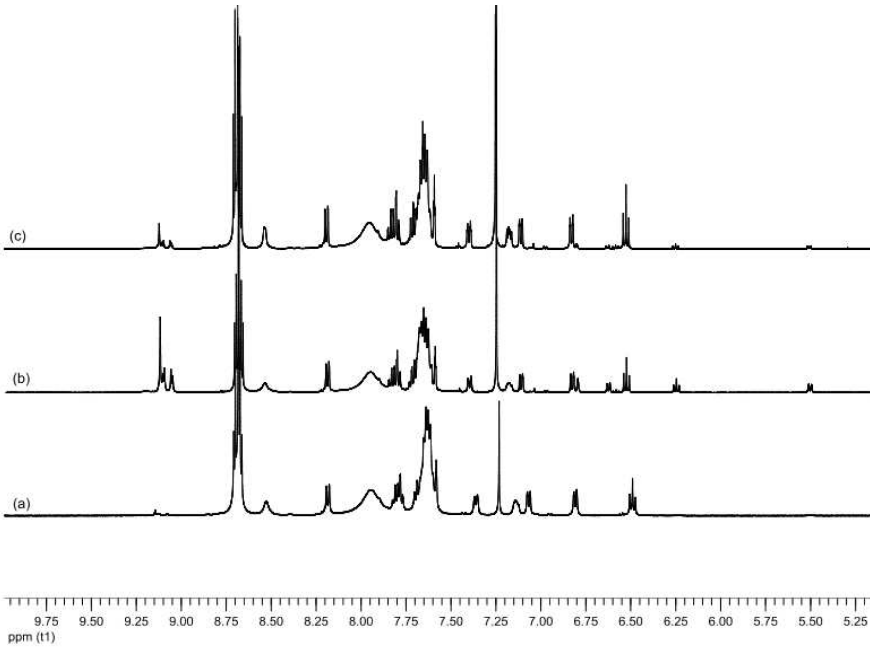


Fig. SI1. 1HNMR spectra of 1 before and after irradiation. 1H NMR spectrum of (a) 1 in CDCl3. (b) 1 in CDCl3 after irradiation at 365 nm for 12 hours. (c) 1 in CDCl3 after heating at 70 - 75 °C for 90 minutes followed by irradiation at 365 nm.

Table 1 Molecular orbital energy levels from DFT calculation for *cis* and *trans* configuration of azopyridine tethered Ni-porphyrin **1**.

	Cis configuration				*Trans* configuration		
231	L+9	−0.71 eV	A	231	L+9	−0.65 eV	A
230	L+8	−0.75 eV	A	230	L+8	−0.7 eV	A
229	L+7	−0.79 eV	A	229	L+7	−0.74 eV	A
228	L+6	−1.07 eV	A	228	L+6	−0.98 eV	A
227	L+5	−1.2 eV	A	227	L+5	−1.15 eV	A
226	L+4	−1.37 eV	A	226	L+4	−1.17 eV	A
225	L+3	−1.48 eV	A	225	L+3	−1.5 eV	A
224	L+2	−2.48 eV	A	224	L+2	−2.46 eV	A
223	L+1	−2.55 eV	A	223	L+1	−2.49 eV	A
222	LUMO	−2.58 eV	A	222	LUMO	−2.85 eV	A
221	HOMO	−5.47 eV	A	221	HOMO	−5.33 eV	A
220	H−1	−5.56 eV	A	220	H−1	−5.46 eV	A
219	H−2	−6.19 eV	A	219	H−2	−6.16 eV	A
218	H−3	−6.3 eV	A	218	H−3	−6.19 eV	A
217	H−4	−6.32 eV	A	217	H−4	−6.39 eV	A
216	H−5	−6.54 eV	A	216	H−5	−6.53 eV	A
215	H−6	−6.76 eV	A	215	H−6	−6.76 eV	A
214	H−7	−6.9 eV	A	214	H−7	−6.79 eV	A
213	H−8	−7.06 eV	A	213	H−8	−6.87 eV	A
212	H−9	−7.13 eV	A	212	H−9	−6.96 eV	A
211	H−10	−7.2 eV	A	211	H−10	−6.99 eV	A

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