Supplementary Information for:
Tuning the Electronic Properties of Phenazine and Bisphenazine Derivatives: A Theoretical and Experimental Investigation

Kathleen A. Robins, Kyoungmi Jang, Bin Cao, and Dong-Chan Lee**

Department of Chemistry, University of Nevada Las Vegas, 4505 S. Maryland Pkwy, Las Vegas, Nevada 89154-4003

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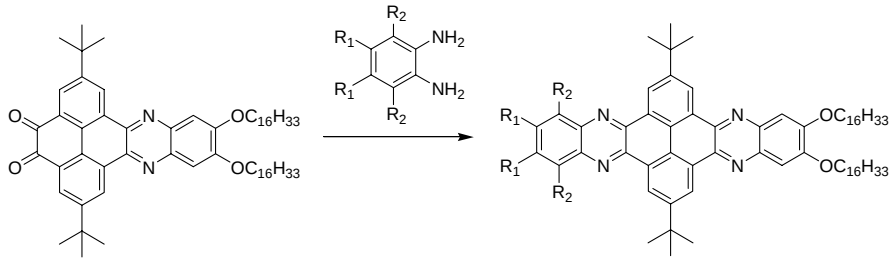
General Instrumentation: Nuclear magnetic resonance (NMR) spectra were obtained with a Varian Gemini 400 MHz NMR spectrometer at room temperature. Deuterated chloroform ($CDCl_3$) containing tetramethylsilane (TMS) as internal standard was used as the solvent for both ^1H NMR and ^{13}C NMR. The low resolution (LR)-EI, LR-ESI, and LR-MALDI mass spectra were recorded at the University of Illinois at Chicago. Optical properties of the molecules were obtained with Shimadzu UV-2450 UV-visible spectrophotometer. Electrochemistry measurements were performed with CV on a CH instrument 660C with a three electrode configuration, with a cell equipped with a platinum plate as the counter electrode, a platinum disc as the working electrode (2 mm diameter), and a non aqueous Ag/Ag^+ electrode (Ag in 10 mM $AgNO_3$ solution in acetonitrile) as the reference electrode. CV measurements for all compounds were recorded in methylene chloride solution containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. All solutions were purged with Ar for 15 - 20 min before each experiment, and a blanket of Ar gas was used during the experiments. The scan rate (ν) was adjusted to 100 mV/s for all experiments. All potentials were calibrated to the ferrocene/ferrocenium (Fc/Fc^+) redox couple.

Synthesis and characterization of compounds: All chemicals and solvents were purchased from commercial source and used as received without further purification. Compounds **P-H$_C$**,[1] **P-F$_A$**,[1] **P-Cl$_A$**,[1] **P-Br$_A$**,[1] **P-Br$_B$**,[1] **BP-H$_C$**,[2] **BP-F$_A$**,[2] **BP-Br$_B$**,[3] **BP-NO$_{2A}$**,[2] and 1,2-diamino-4,5-dibromobenzene[4] were synthesized according to the literature procedures.

P-Cl$_C$ To a suspension of 1,2-dinitrotetrachlorobenzene (500 mg, 1.64 mmol) in 20 mL absolute ethanol and 5 mL HCl was added tin powder (660 mg, 5.56 mmol). The mixture was stirred for 3 hr at room temperature and the mixture was warmed to 45 ^oC for additional 1.5 hr with stirring. The resulting reaction mixture was poured into ethyl acetate, and saturated $NaHCO_3$ was added followed by 0.5 M Na_2S solution. The separated organic layer was dried over sodium sulfate (Na_2SO_4), and filtered with ethyl acetate. The remaining solvent was removed under vacuum. By evaporating solvent, white crystal was obtained and the obtained 1,2-diamino-3,4,5,6-tetrachlorobenzene was used for next reaction without any further purification (yield: 95%). 1,2-Diamino-3,4,5,6-tetrachlorobenzene (385 mg, 1.57 mmol) was dissolved in 30 mL absolute ethanol. 2,5-Dihydroxy-1,4-benzoquinone (220 mg, 1.57 mmol) was added at once and the mixture was refluxed for 24 hours under a positive N_2 flow. After evaporating the solvent, without purification of the intermediate, the crude solid was dissolved in 30 mL *N*,*N*-dimethylformamide (DMF), followed by addition of potassium carbonate (K_2CO_3) (760 mg, 5.50 mmol). Then bromodecane (0.98 mL, 4.71 mmol) was added and the mixture was maintained at 60 ˚C. During reaction, same amount of K_2CO_3 and bromodecane was added twice by following TLC result for 5 days with continuous stirring. The mixture was cooled down to room temperature and poured into H_2O, filtered and washed thoroughly with H_2O. It was then dried over anhydrous sodium sulfate. The product was purified by silica gel column chromatography (CH_2Cl_2/Hexane 1/2 v/v). The pure product was obtained as a yellow solid. (Two-step yield: 12%). ^1H NMR ($CDCl_3$) δ 7.45 (s, 2H), 4.25 (t, 4H, J = 6.6 Hz), 1.97 (m, 4H), 1.5-1.2 (m, 28H), 0.89 (t, 6H, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 156.14, 142.54, 137.16, 132.01, 130.80, 105.46, 69.75, 31.93, 29.61, 29.57, 29.35, 29.33, 28.71, 26.00, 22.70, 14.12. LR-EI-MS calcd for $C_{32}H_{44}Cl_4N_2O_2$ m/z = 628.22, found m/z = 628.39 $[M]^+$

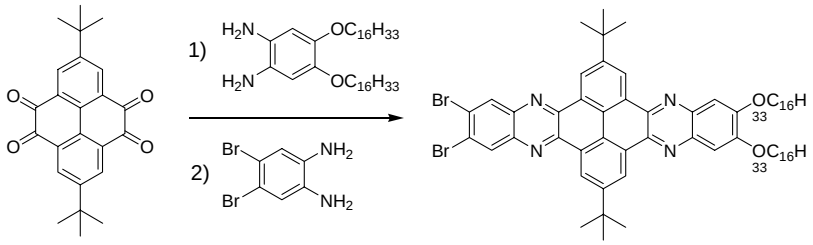


A

BP-Cl$_A$: R_1 = Cl, R_2 = H
BP-Cl$_C$: R_1 = R_2 = Cl

BP-Cl$_A$ The intermediate **A**[2,3] (190 mg, 0.21 mmol) was dissolved in 40 mL chloroform ($CHCl_3$) and 10 mL acetic acid (AcOH). To that solution, 1,2-diamino-4,5-dichlorobenzene (40 mg, 0.23 mmol) was added. The reaction mixture was refluxed overnight under a positive N_2 flow. After cooling it to room temperature, the reaction mixture was extracted with H_2O and 10% aqueous sodium hydroxide (NaOH) solution. The organic layer was dried over Na_2SO_4, and filtered with hot $CHCl_3$. The remaining solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2/hexane 1/3 to 1/1) to give the pure product as a yellow solid (yield: 55%). ^{1}H NMR ($CDCl_3$) δ 9.73 (d, 2H, *J* = 2 Hz), 9.64 (d, 2H, *J* = 2 Hz), 8.50 (s, 2H), 7.58 (s, 2H), 4.32 (t, 4H, *J* = 6.8 Hz), 2.02 (m, 4H), 1.75 (s, 18H), 1.61 (m, 4H), 1.5-1.2 (m, 48H), 0.88 (t, 6H, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 153.34, 150.55, 143.89, 140.61, 140.03, 139.95, 133.95, 129.75, 129.64, 128.47, 125.08, 124.26, 123.77, 106.81, 69.21, 35.88, 31.95, 31.91, 29.78, 29.75, 29.71, 29.51, 29.40, 28.99, 26.14, 22.71, 14.13 (5 aliphatic peaks not seen due to overlapping signals). LR-MALDI-MS calcd for $C_{68}H_{92}Cl_2N_4O_2$ *m/z* = 1066.66, found *m/z* = 1066.95 $[M]^+$

BP-Cl$_C$ The intermediate A (296 mg, 0.32 mmol) was dissolved in 20 mL $CHCl_3$ and 5 mL AcOH. To that solution, 1,2-diamino-3,4,5,6-tetrachlorobenzene (80 mg, 0.333 mmol) was added. The reaction mixture was refluxed overnight under a positive N_2 flow. After cooling it to room temperature, the reaction mixture was extracted with H_2O and 10% aqueous NaOH solution. The organic layer was dried over Na_2SO_4, and filtered with hot $CHCl_3$. The remaining solvent was removed under vacuum. The crude product was purified by silica gel column chromatography (eluent: CH_2Cl_2/ hexane 1/3) to give the pure product as a yellow solid (yield: 67%). ^{1}H NMR ($CDCl_3$) δ 9.78 (d, 2H, *J* = 2 Hz), 9.75 (d, 2H, *J* = 2 Hz), 7.59 (s, 2H), 4.33 (t, 4H, *J* = 6.8 Hz), 2.03 (m, 4H), 1.76 (s, 18H), 1.61 (m, 4H), 1.5-1.2 (m, 48H), 0.88 (t, 6H, *J* = 7 Hz). ^{13}C NMR ($CDCl_3$) δ 153.43, 150.82, 144.03, 140.00, 139.89, 137.56, 133.15, 131.62, 129.80, 127.88, 125.36, 125.05, 124.38, 106.81, 69.24, 35.83, 31.95, 31.82, 29.77, 29.75, 29.70, 29.49, 29.39, 28.98, 26.14, 22.71, 14.13 (5 aliphatic peaks not seen due to overlapping signals). LR-ESI-MS calcd for $C_{68}H_{90}Cl_4N_4O_2$ *m/z* = 1134.58, found *m/z* = 1135.6 $[M+H]^+$ LR-MALDI-MS calcd for $C_{68}H_{90}Cl_4N_4O_2$ *m/z* = 1134.58, found *m/z* = 1134.86 $[M]^+$



BP-Br$_A$ 2,7-Di-*tert*-butylpyrene-4,5,9,10-tetraone (414 mg, 1.11 mmol) was suspended in 261 mL $CHCl_3$ and 89 mL AcOH. To that mixture, 1,2-bishexadecyloxy-4,5-diaminobenzene (579 mg, 0.99 mmol) was added at once. The reaction mixture was refluxed under a positive N_2 flow. After 2 hours, 1,2-diamino-4,5-dibromobenzene (322 mg, 1.2 mmol) was added into the reaction mixture and the mixture was refluxed for an additional 2 hours under a positive N_2 flow. After cooling it to room temperature, the reaction mixture was extracted with water to remove AcOH, and the organic layer was neutralized by saturated sodium bicarbonate ($NaHCO_3$) solution. The organic layer was then dried over Na_2SO_4, and the solvent was evaporated after filtration. The crude material was purified by silica gel column chromatography (eluent: chloroform/hexane 1/3 to 1/1) to give the pure product as a yellow solid (Two-step yield: 25%). ^{1}H NMR ($CDCl_3$) δ 9.76 (d, 2H, *J* = 2.4 Hz), 9.67 (d, 2H, *J* = 2.0 Hz), 8.75 (s, 2H), 7.62 (s, 2H), 4.33 (t, 4H, *J* = 6.6 Hz), 2.03 (m, 4H), 1.75 (s, 18H), 1.61 (m, 4H), 1.5-1.2 (m, 48H), 0.88 (t, 6H, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$) δ 153.42, 150.66, 144.07, 141.16, 140.11, 140.02, 133.26, 129.73, 128.57, 126.03, 125.20, 124.35, 123.88, 106.86, 69.25, 35.88, 31.94, 31.90, 29.76, 29.75, 29.69, 29.49, 29.39, 28.99, 26.14, 22.71, 14.13 (5 aliphatic peaks not seen due to overlapping signals). LR-MALDI-MS calcd for $C_{68}H_{92}Br_2N_4O_2$ *m/z* = 1154.56, found *m/z* = 1154.92 $[M]^+$

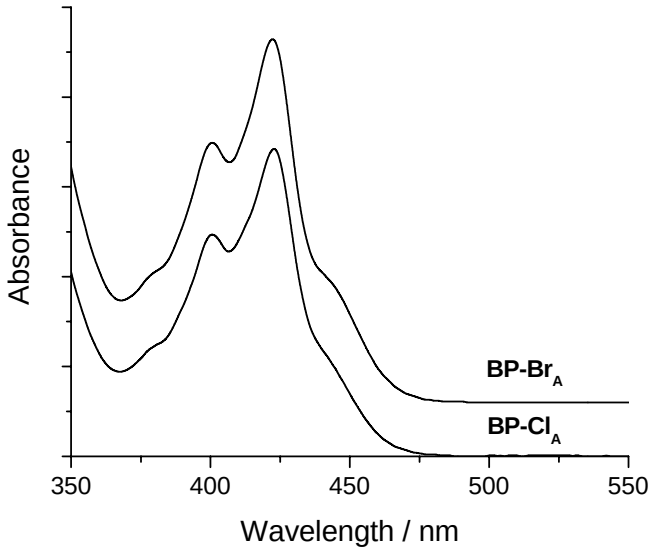


Figure S1. UV-vis spectra of **BP-Cl$_A$** and **BP-Br$_A$** in $CHCl_3$.

References

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