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Synthesis and Utilization of Perylene-based *n*-type Small Molecules in Light-Emitting Electrochemical Cells

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Supporting Information Available

I) Synthesis of Perylene Compounds
II) Cyclic Voltammetry

I) Synthesis of Perylene Compounds

General Details: UV/Vis spectra were acquired using an Agilent 8453 spectrometer fitted with a Model 809090A temperature control unit. Compounds were verified on either a Brucker-AV300 operating at 300 MHz or 301MHz for both ^{1}H and ^{13}C, as well a High Resolution Mass Spectrometry on a Bruker APEX Qe 47e. Photoluminescence spectra of thin films of **3** were obtained on a Horiba Jobin Yvon Fluorolog Model FL-1039.

1,6,7,12-tetrabromo-perylene-3,4,9,10-tetracarboxylic dianhydride (1). 27.7 grams of perylene-3,4,9,19-tetracarboxylic dianhydride was placed in a 500 mL flask. To this was added 300 mL of 98% H_2SO_4. This was allowed to stir for 2 days, after which the reaction was heated to 65 °C and I_2 (0.58g, 2.29 mmol) was added. The reaction was then heated to 85 °C. A water condenser was placed on the flask along with a liquid addition funnel and air lock. Br_2 (15.5mL, 302.51 mmol) was added slowly, 1 drop every 5 second, while the reaction stirred for 19 hours. The reaction was then heated to 110 °C and more Br_2 (6.7 mL, 130.76 mmol) was added to the funnel. The reaction was allowed to stir for 5 days. The reaction was then cooled to room temperature and N_2 gas was bubbled through the reaction while stirring to remove excess Br_2. The reaction was then slowly poured in to 100 mL of ice water, Br_2 gas evolved during this process. The precipitate was collected via suction filtration and rinsed with 2 L of DI water. The resulting red powder was then place in a vacuum oven overnight at 105 °C. (21.58g, >50% yield). HRMS (ESI) *m/z*: , calcd for $C_{25}H_8Br_4Na_1O_7$ 758.6896, found 758.6924.

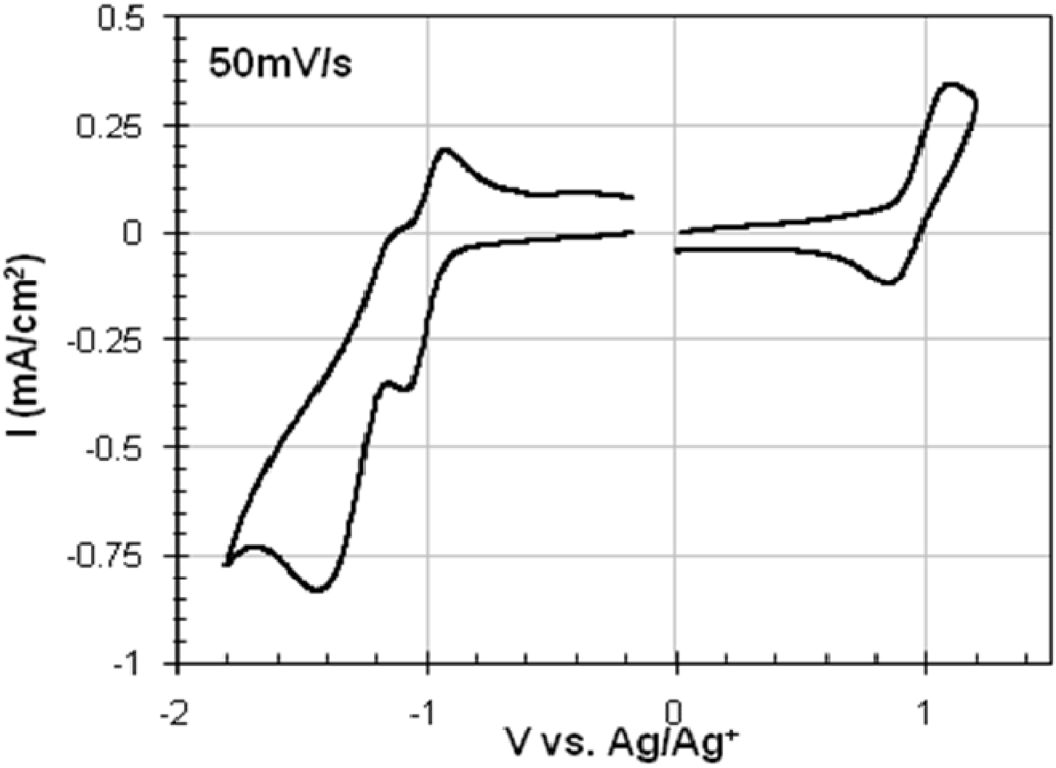
1,6,7,12-tetrabromo-N,N'-bis-(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) (2). Combined **1** (2 g, 2.82 mmol) with 50 mL of propionic acid in a flame dried 100 mL two-neck flask with a water condenser, under argon. Reaction was stirred and heated to 140 °C. Once at 140 °C, 2.6-diisopropyl aniline (3.3 mL, 16.92 mmol) was added via syringe. This was allowed to stir overnight. The propionic acid was then removed by vacuum distillation. Some propionic acid still remained so the product was dissolved in 25 mL of CH_2Cl_2 and washed with 10 mL of 1 M NaOH. The organic layer was then drained and set aside while the aqueous layer was extracted 3 x 25ml CH_2Cl_2. The organic layers were combined, dried over $MgSO_4$, and the solvent was removed to yield a red powder. Purification on silica eluted with 30% CH_2Cl_2 in hexanes, followed by recrystallization from CH_2Cl_2/hexanes yielded a bright reddish orange powder (0.957 g, 33%). ^{1}H NMR (CDCl3) δ 8.90 (s, 4H), 7.52 (t, *J*=7.5 Hz, 2H), 7.36 (d, *J*=7.5 Hz, 4H), 2.74 (S, *J*=6.9 Hz, 4H), 1.194 (d, *J*=2.4 Hz, 12H), 1.162(d, *J*=2.1 Hz,12H) . ^{13}C NMR

(CDCl3) δ 162.607, 145.948, 136.932, 132.353, 132.078, 130.212, 124.938, 124.627, 124.562, 123.009, 29.613, 24.399. HRMS (ESI) *m/z*: , calcd for $C_{48}H_{38}Br_4N_2Na_1O_4$ 1044.9457, found 1044.9493.

1,6,7,12-tetra(4-tert-butyl-phenoxy)-N,N'-bis-(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) (3). Combined 4-tert-butylphenol (1.81 g, 12 mmol) with 5 mL of N-methyl-2-pyrolidinone in a flame dried 50 mL two-neck flask with a water condenser, under argon. Placed in an ice bath and stirred untill the butylphenol was dissolved. 0.272 g of CaH_2 (6 mmol) was added. After 30 minutes **2** (0.6g, 0.6 mmol) was added and the reaction was heated to 130 ^{o}C. Reaction was stirred for 20 hours then removed from heat. Once cool, 25 mL of water was added to the reaction and was extracted 3 x 25ml toluene. The organic phases were combined then washed 3 x 50 mL 1 M HCl and dried over $MgSO_4$. Removal of the solvent left a damp, dark red powder. Purification on silica eluted with 2:5 CH_2Cl_2/hexanes yielded a bright red powder. (0.187g, 23%). ^{1}H NMR (CDCl3) δ 8.32 (s, 4H), 7.43 (t, *J*=7.8 Hz, 2H), 7.28 (m, 12H), 6.90 (d, *J*=8.7 Hz, 8H), 2.74 (S, *J*=6.6 Hz, 4H), 1.30 (s, 36H), 1.15 (d, *J*=6.6 Hz, 24H). ^{13}C NMR (CDCl3) δ 163.55, 156.12, 153.00, 147.55, 145.82, 133.45, 130.90, 129.60, 126.88, 124.08, 122.91, 120.98, 120.45, 120.39, 119.42, 34.58, 31.66, 29.29, 24.24. HRMS (ESI) *m/z*: calcd for $C_{88}H_{90}N_2Na_2O_8$ 674.3241, found 674.3255.

II) Cyclic Voltammetry

To determine the band gap of **3**, electrochemistry experiments were performed using an electrolyte solution of 0.1 **M** tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) and 0.1 m**M** of the perylene compound in anhydrous acetonitrile/chloroform (50:50). All solutions in the cell were purged with high-purity nitrogen for five to ten minutes before each experiment, and a blanket of nitrogen was used during the experiment. Electrochemical experiments employed a platinum wire counter electrode and a non-aqueous silver/silver ion reference electrode (0.1 M $AgNO_3$ solution, Ag/Ag^{+}, 0.25 V vs. SCE). Electrochemical data was obtained on a Princeton Applied Research Potentiostat Model 362.



Solution CV of 3 in 0.1M TBAP in CHCl3/acetonitrile at 50mV/s