SUPPORTING INFORMATION

Poly(acenaphtho[1,2-b]thieno[3,4-e]pyrazine): A New Low Band Gap Conjugated Polymer

Jon P. Nietfeld, Christopher L. Heth, and Seth C. Rasmussen*

Department of Chemistry and Molecular Biology, North Dakota State University, Fargo, ND 58105, USA. Fax: 1-701-231-8747; Tel: 1-701-231-8831; E-mail: seth.rasmussen@ndsu.edu

Table of Contents:

General. 3,4-Diaminothiophene (**8**)[1] was prepared from the reduction of 2,5-dibromo-3,4-dinitrothiophene[2] as previously reported. Unless otherwise specified, all reactions were carried out under nitrogen atmosphere with reagent grade materials. Chromatographic separations were performed using standard column methods with silica gel (230-400mesh). The ^{1}H and ^{13}C NMR spectra were carried out on a 400 MHz spectrometer in CDCl$_3$. All NMR data was referenced to the chloroform signal and peak multiplicity was reported as follows: s = singlet, d = doublet, t = triplet.

Acenaptho[1,2-b]thieno[5,4-e]pyrazine (10). Diaminothiophene **8** (1.3 g, 11.4 mmol) was dissolved in 80mL of absolute ethanol. 1,2-Acenapthenequinone (2.5 g, 13.7mmol) was then added and the solution heated at reflux for 3 hours. The mixture was then cooled to room temperature, diluted with 200 mL of water, and extracted with dichloromethane. The combined organic layers were dried with anhydrous Na$_2$SO$_4$ and the solvent removed by rotary evaporation. The resulting solid was then dissolved in CH$_2$Cl$_2$,

run through a 5 cm silica plug, and concentrated to give a yellow solid. A final recrystallization from methanol gave yellow needles of **10** (1.6 g, 54%). mp: ~150 °C (dec); ^{1}H NMR: δ 8.25 (dd, J = 7.2, 0.4 Hz, 2H), 8.03 (dd, J = 8.4, 0.4 Hz) 2H), 7.98 (s, 2H), 7.77 (dd, J = 8.4, 7.2 Hz, 2H); ^{13}C NMR: δ 154.5, 142.1, 138.5, 131.7, 130.4, 129.3, 128.9, 121.1, 117.8.
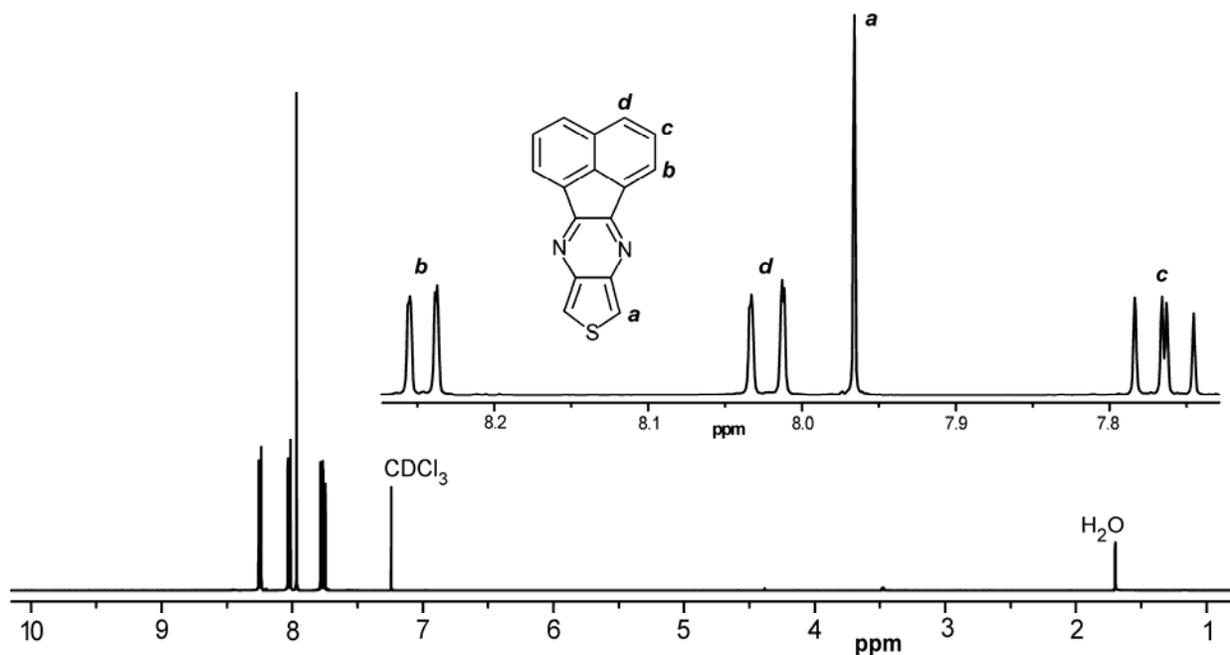
Figure S1. ^{1}H NMR spectrum of monomer **10**
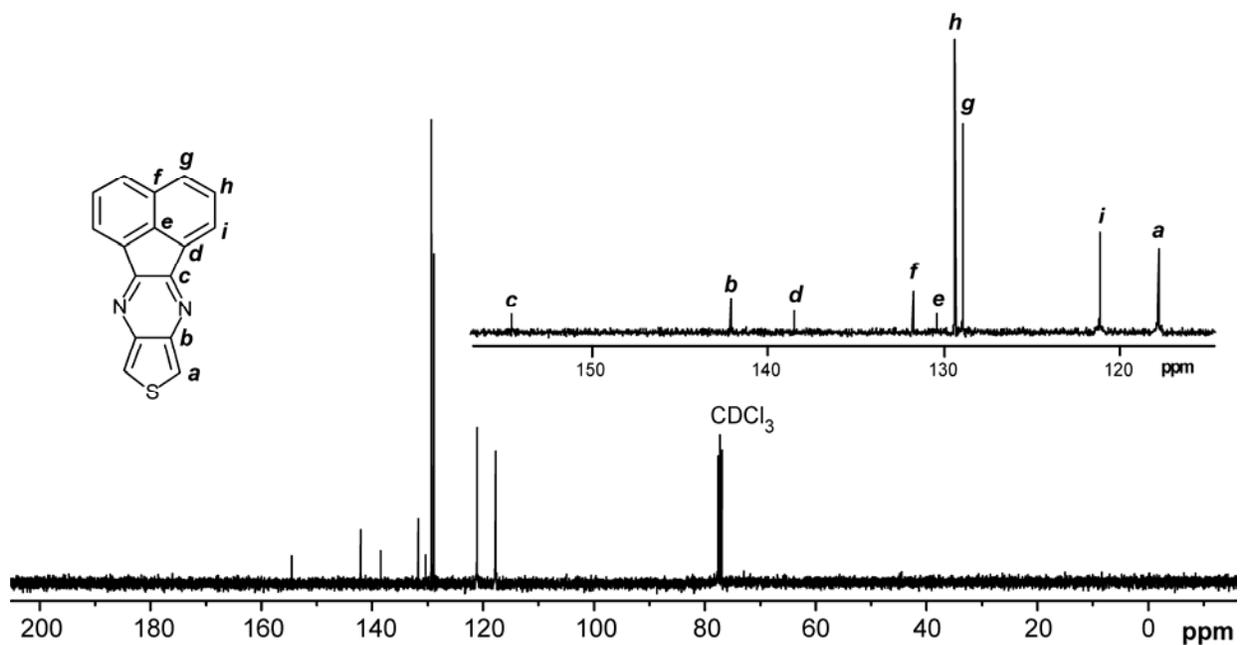
Figure S2. ^{13}C NMR spectrum of monomer **10**

Electrochemistry and Electropolymerizations. Electropolymerization experiments were carried out in a three-electrode cell consisting of a working electrode (either a platinum disc or an indium tin oxide (ITO) coated slide), a platinum wire auxiliary electrode, and a silver wire quasi-reference electrode. Solutions consisted of monomer **10** (0.06 M) dissolved in anhydrous CH_2Cl_2 with 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte. The solutions were deoxygenated by sparging with argon prior to each scan and blanketed with argon during the polymerizations. The platinum disc working electrode was polished with 0.05 mm alumina and washed well with deionized water and dry CH_2Cl_2 prior to each film growth. The polymer films were grown at a constant potential of 1.75 V. The resulting polymer films were then conditioned by cycling several times. The polymer-coated electrode was then removed, washed with dry CH_2Cl_2 and placed in a cell with a fresh electrolyte solution. Cyclic voltammetry (CV) were carried out in the cell described above at a sweep rate of 100 mV/s. The solutions were argon sparged and blanketed as described above. Potentials were referenced to the ferrocene redox couple (45 mV vs. Ag/Ag^+).

Differential pulse voltammetry (DPV) was performed on electropolymerized films of pATP for additional determination of the redox onsets. Measurements were of the pATP films on a platinum disc working electrode. Conditions and cell configuration were the same as for the CV measurements above, with the exception that the sweep rate was reduced to 20 mV/s. Both positive and negative sweeps were measured in order to determine accurate onsets for both the oxidation and reduction of the polymer film.

Analysis of monomer **10** by CV was carried out in the cell described above, substituting a Ag/Ag^+ reference electrode (0.251 V vs. SCE)[3] for the silver wire quasi-reference. Solutions consisted of monomer (0.06 M) dissolved in spectral grade CH_3CN with 0.10 M $TBAPF_6$ as the supporting electrolyte. All scans were performed at a sweep rate of 100 mV/s and solutions were argon sparged and blanketed as described above.
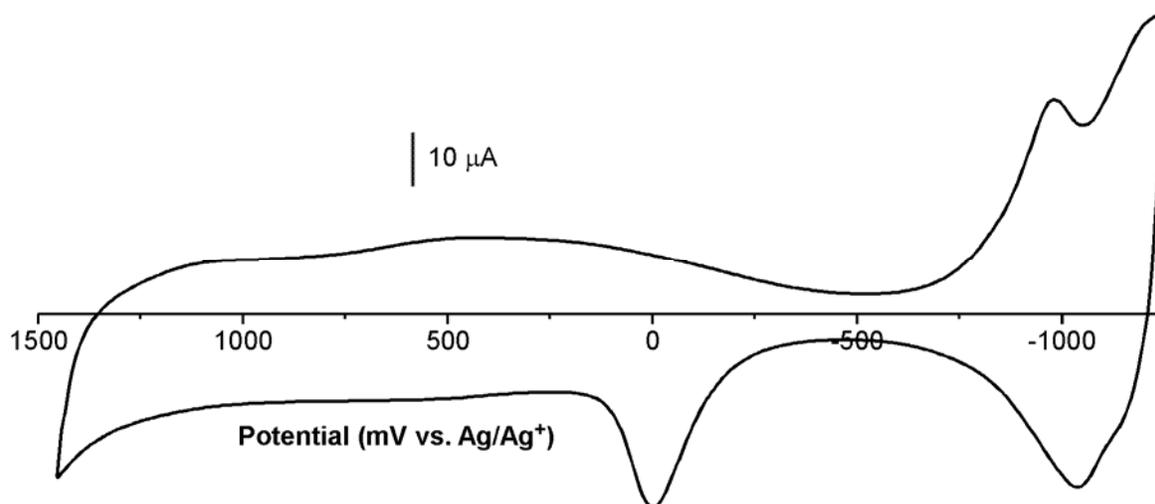
Figure S3. Expanded CV of pATP

MO and ZINDO Calculations. All calculations were performed using the Gaussian03 software package. Optimized geometries were calculated unrestrained using HF methods and the 6-31G* basis set. Single point energy calculations were then performed using the same methods as the geometry optimization, followed by ZINDO calculations to determine transition energies. For neutral species, a single point energy calculation using methods matching the geometry optimization followed. Mulliken spin densities for radical species were determined from a single point energy calculation at the neutral optimized geometry using DFT methods, a 6-31G* basis set, and a B3LYP correlation functional. Molecular orbital diagrams were generated using GaussView 3.09 from the checkpoint file generated during the single point energy calculations. In all calculations, very tight SCF convergence criteria were used and molecular symmetry was ignored. When stepwise calculations were performed, the trailing step used only the output geometry from the previous step and did not glean a guess from a previous checkpoint file.
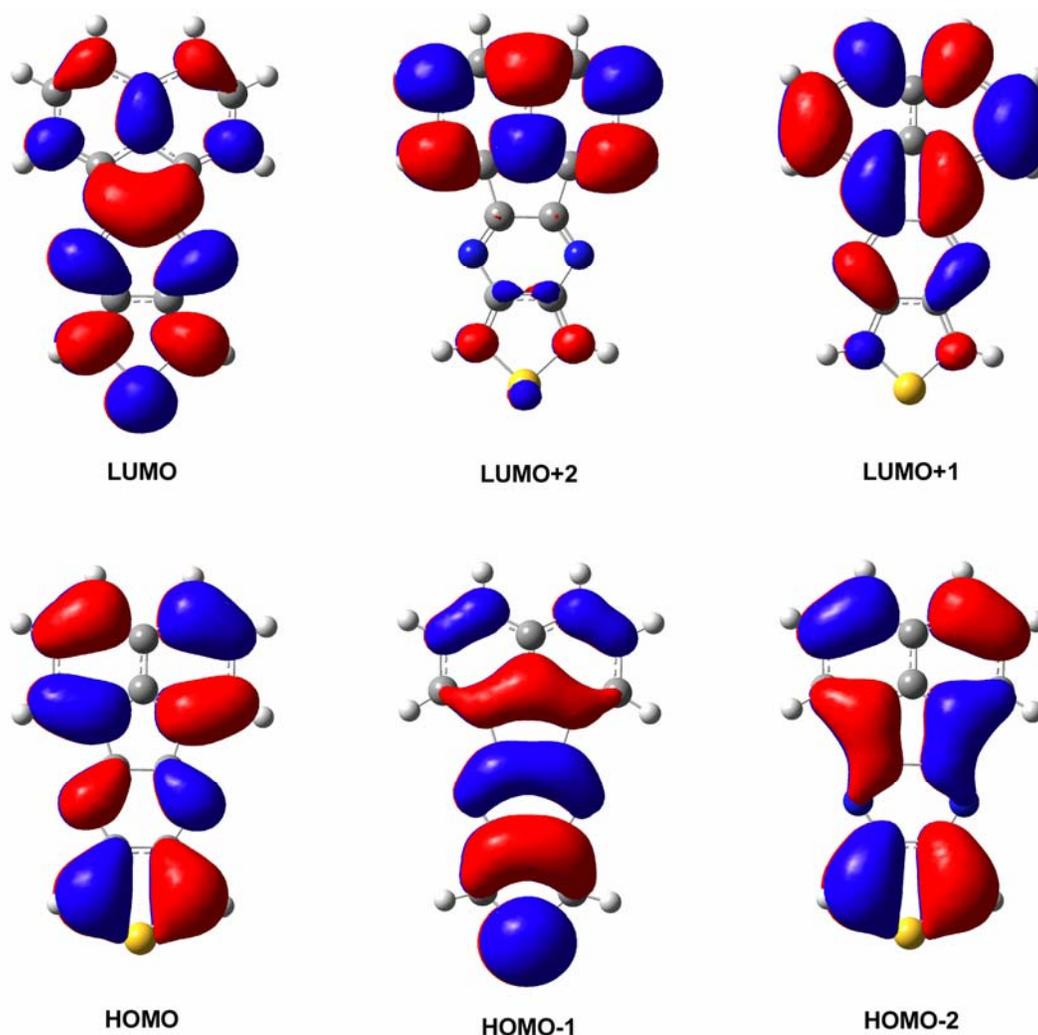
Figure S4. MOs of monomer **10**

Table S1. Mulliken atomic charges for the radical cation of monomer **10**
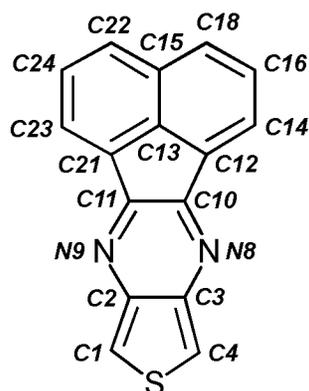
Atom	Atomic Charge	Atom	Atomic Charge
C1	0.270927	C15	-0.049852
C2	-0.044499	C16	-0.007459
C3	-0.044517	H17	-0.002903
C4	0.270884	C18	0.149767
S5	-0.044427	H19	-0.000453
H6	-0.012052	H20	-0.006053
H7	-0.012052	C21	0.099461
N8	0.103935	C22	0.149796
N9	0.103942	23 C	0.055183
C10	-0.042094	24 C	-0.007473
C11	-0.042079	25 H	-0.006053
C12	0.099453	26 H	-0.002906
C13	-0.033161	27 H	-0.000453
C14	0.055140		

Table S2. Calculated HOMO-LUMO energy gaps of $(ATP)_n$ oligomers

n	HOMO-LUMO		n	HOMO-LUMO	
	nm	eV		nm	eV
1	327	3.79	4	795	1.56
2	560	2.21	8	1017	1.22
3	692	1.79			
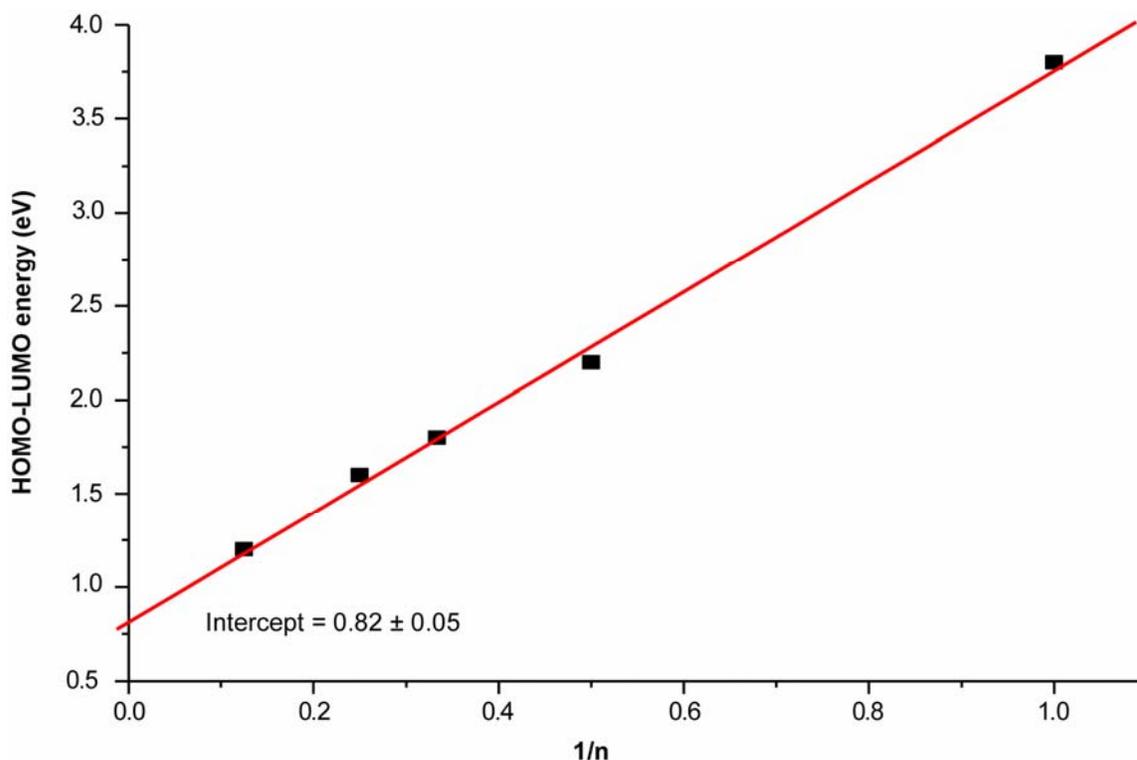
Figure S5. Plot of 1/n vs. HOMO-LUMO energy

Table S3. ZINDO results for the octamer (ATP)$_8$

Transition	eV	nm	f
1	1.22	1017	1.73
2	1.90	654	0.15
3	2.45	507	0.25
4	2.77	448	0.38
5	2.82	439	0.73
6	2.94	422	0.27

Optical Spectroscopy and Spectroelectrochemistry. Visible-NIR spectroscopy was performed on a dual beam scanning UV-vis-NIR spectrophotometer using polymer samples grown on ITO slides as stated above. After polymerization, the polymer-coated electrode was held at a reducing potential to ensure dedoping of the film. The film was then washed with CH_2Cl_2 and dried. Spectroscopy was conducted on the films with reference to blank ITO slides.

Spectroelectrochemistry was performed in a 1-cm quartz cuvette equipped with a polymer- coated ITO working electrode, a platinum wire auxiliary electrode, and a silver wire quasi-reference electrode. The

cell solution consisted of 0.1 M TBAPF$_6$ in dry CH$_2$Cl$_2$. The ITO slide/polymer film was held at the desired potential for 120 seconds before measurement of the spectrum.

REFERENCES

1. D. D. Kenning, K. A. Mitchell, T. R. Calhoun, M. R. Funfar, D. J. Sattler, and S. C. Rasmussen, *J. Org. Chem.*, 2002, **67**, 9073.

2. L. Wen and S. C. Rasmussen, *J. Chem. Crystallogr.*, 2007, **37**, 387.

3. R. C. Larson, R. T. Iwamoto, and R. N. Adams, *Anal. Chim. Acta,* 1961, **25**, 371.