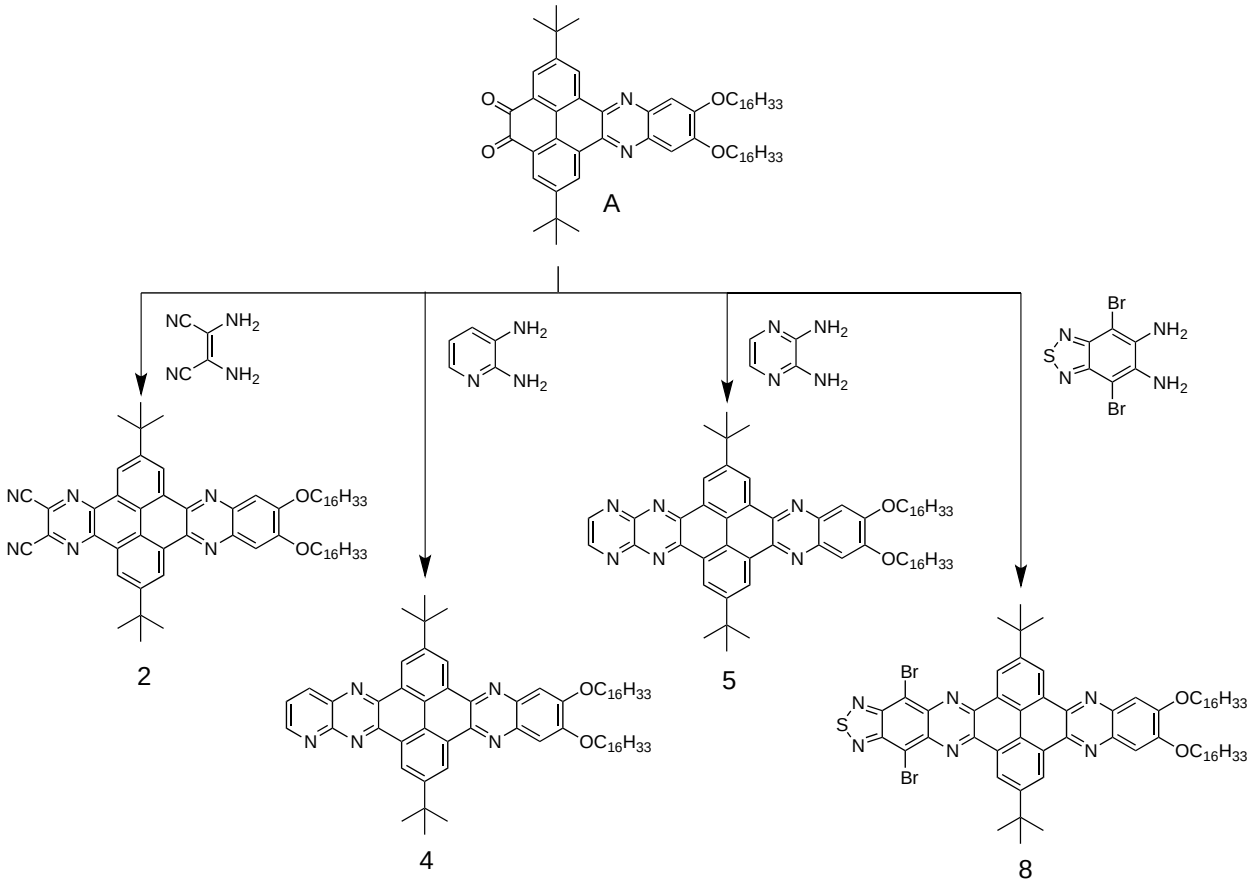
Supplementary Information for:
Controlling the Electron-Deficiency of Self-Assembling Pyrazine-Acenes: A Collaborative Experimental and Theoretical Investigation

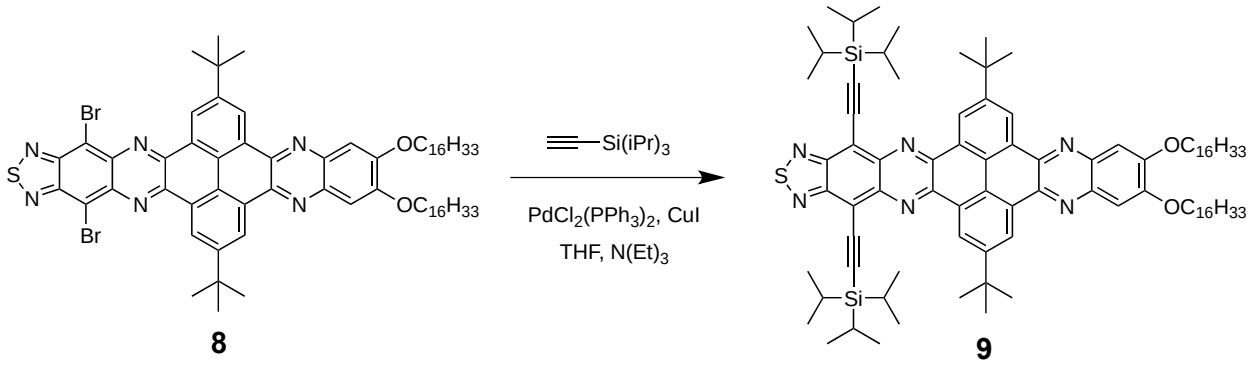
*Lacie V. Brownell, Kyoungmi Jang, Kathleen A. Robins, Ich C. Tran, Clemens Heske, and Dong-Chan Lee**

Department of Chemistry, University of Nevada Las Vegas, 4505 S. Maryland Pkwy, Box454003, Las Vegas, Nevada 89154-4003, USA

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 an internal reference was used as the solvent for both ^1H NMR and ^{13}C NMR. Optical properties of the molecules were obtained with Shimadzu UV-2450 UV-Visible spectrophotometer and Horiba Fluorimeter using a xenon lamp excitation source for absorption and fluorescence emission, respectively. Electrochemistry measurements were performed with cyclic voltammetry (CV) on a CH instrument 660D 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 nonaqueous Ag/Ag^+ electrode (Ag in 10 mM $AgNO_3$ solution in anhydrous acetonitrile) as the reference electrode. CV measurements for all compounds were recorded in a 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 positive pressure of Ar was maintained over the sample solution during the experiments. The scan rate was $\nu = 100$ mV/s for all experiments. All potentials are reported versus the ferrocene/ferrocenium (Fc/Fc^+) redox couple which was used as an internal standard. Atomic force microscopy (AFM) was performed using the non-contact AFM mode on a Park XE-70 in-air scanning probe microscopy system with an NCHR cantilever.



Scheme S1. Reaction routes to compounds **2**, **4**, **5**, and **8**.



Scheme S2. Synthesis of **9** via Sonagashira coupling of **8** with TIPSA.

Experimental procedures

Intermediate **A**[1] and 4,7-dibromo-benzo[1,2,5]thiadiazole-5,6-diamine[2] were prepared according to previously published procedures.

Compound **2**

To a round bottom flask containing 0.216 mmol of intermediate **A**, acetic acid (10 mL) was

added. To the mixture, 0.259 mmol of maleonitrile was added. The resulting solution was stirred, under a nitrogen atmosphere, at 110 °C for 12 hours. An additional 0.259 mmol of maleonitrile was added to the reaction flask, and stirring continued at 110 °C for an additional 12 hours. Crude product was obtained by extracting with methylene chloride and washing with $NaHCO_3$ followed by water. The organic layers were combined and dried over sodium sulfate. The product was purified by silica gel column chromatography (30 / 70 methylene chloride / hexane) providing a yield of 56%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.65 (2H, d, *J*=2.0 Hz), 9.25 (2H, d, *J*=1.8 Hz), 7.48 (2H, s), 4.31 (4H, t, *J*=6.6 Hz), 2.04 (4H, m), 1.72 (18H, s), 1.58 (4H, m), 1.45 (4H, m), 1.26 (44H, s), 0.88 (6H, t, *J*=6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.60, 151.18, 143.27, 139.89, 138.90, 129.85, 129.39, 125.89, 125.64, 125.07, 123.92, 114.15, 106.56, 69.30, 35.91, 31.94, 31.83, 29.78, 29.76, 29.71, 29.70, 29.50, 29.39, 29.01, 26.15, 22.70, 14.13. $[M+H]^+$: Calcd 999.7; Found 999.7.

Compound **4**

To a round bottom flask containing 0.216 mmol of intermediate **A**, cholorform (8.4 mL) and acetic acid (2.7 mL) were added. 0.216 mmol of 2,3-diaminopyridine was added to the flask lastly. The resulting solution was stirred, under a nitrogen atmosphere, at 80°C for 20 hours. Precipitates obtained after cooling the reaction solution were filtered and rinsed with $NaHCO_3$, H_2O, and then methanol. The product was purified by silica gel column chromatography (60 / 40 methylene chloride / hexane) providing a yield of 85%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.90 (1H, d, *J*=2.2 Hz), 9.79 (2H, overlapping doublets), 9.72 (1H, d, *J*=2.2 Hz), 9.34 (1H, dd, *J*=4.0, 1.9), 8.80 (1H, dd, *J*=8.4, 2.0 Hz), 7.85 (1H, dd, *J*=8.4, 3.9 Hz), 7.62 (2H, d, *J*=1.8 Hz), 4.33 (4H, t, *J*=6.7 Hz), 2.01 (4H, m), 1.74 (18H, s), 2.02 (4H, m), 1.61 (4H, m), 1.42 (4H, m), 1.26 (44H, s), 0.88 (6H, t, *J*=6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.32, 150.92, 143.01, 139.58, 138.51, 129.72, 129.11, 125.71, 125.39, 124.71, 123.14, 114.14, 106.32, 69.21, 35.86, 31.96, 31.84, 29.80, 29.77, 29.74, 29.71, 29.53, 29.40, 29.02, 26.15, 22.72, 14.14. $[M+H]^+$: Calcd 1000.7 Found 1000.7.

Compound **5**

To a round bottom flask containing 0.755 mmol of intermediate **A**, chloroform (25 mL) and acetic acid (25 mL) were added. 0.755 mmol of 2,3-diaminopyrazine was added to the flask lastly. The resulting solution was stirred, under a nitrogen atmosphere, at 70 °C for 7 days. Precipitates obtained after cooling the reaction solution were filtered and rinsed with $NaHCO_3$, H_2O, and then methanol. The product was purified by silica gel column chromatography (1 / 99 ethyl acetate / methylene chloride) providing a yield of 18%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.84 (4H, s), 9.30 (2H, s), 7.27 (2H, s), 4.34 (4H, t, *J*=6.6 Hz), 2.03 (4H, m), 1.67 (18H, s), 1.61 (4H, m), 1.46 (4H, m) 1.26 (44H, s), 0.88 (6H, t, *J*=7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.64, 151.23, 148.52, 147.49, 145.10, 140.16, 139.99, 129.97, 128.14, 125.78, 125.45, 106.88, 69.31, 35.98, 31.94, 31.83, 29.75, 29.68, 29.45, 29.38, 28.95, 26.13, 22.70, 14.12. (1 aromatic peak and 7 alkyl peaks not resolved due to overlapping signals) $[M+H]^+$: Calcd 1001.5 Found 1001.8.

Compound **8**

To a round bottom flask containing 0.329 mmol of intermediate **A**, acetic acid (16 mL) was added. 0.494 mmol of 5,6-diamino-4,7-dibromo-2,1,3-benzothiadiazole was added to the flask lastly. The resulting solution was stirred, under a nitrogen atmosphere, at 90 °C for 18 hours.

Precipitates obtained after cooling the reaction solution were filtered and rinsed with $NaHCO_3$, H_2O, and then methanol. The product was purified by silica gel column chromatography (50 / 50 methylene chloride / hexane) providing a yield of 57%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.64 (4H, s), 7.44 (2H, s), 4.29 (4H, t, *J*=7.0 Hz), 2.00 (4H, m), 1.61 (4H, m), 1.47 (4H, m), 1.27 (44H,s), 0.88 (6H, t, *J*=6.4 Hz); ^{13}C NMR was unable to be performed due to poor solubility at concentrations required for ^{13}C NMR measurements. $[M+H]^+$: Calcd 1213.4 Found 1213.4.

Compound **9**

To a round bottom flask containing 0.247 mmol of compound **8** with 8 mol% $PdCl_2(PPh_3)_2$, 45 mL THF and 15 mL triethylamine was added (both were degassed with argon prior to use). 0.741 mmol of (triisopropylsilyl)acetylene was added via syringe and 8 mol% CuI was added lastly. The reaction mixture stirred under nitrogen for 2.5 hours at 65 °C. The resulting mixture was filtered over a silica pad and further purified by column chromatography (30 / 70 methylene chloride / hexane) and recrystallization from hexane and methanol to provide a yield of 19%. ^{1}H NMR (400MHz, $CDCl_3$, ppm): 9.83 (2H, d, *J*=2.0 Hz), 9.76 (2H, d, *J*=2.0 Hz), 7.63 (2H, s), 4.34 (4H, t, *J*=6.6Hz), 2.03 (4H, m), 1.73 (18H, s), 1.61 (4H, m), 1.36-1.26 (90H, overlapping peaks), 0.88 (6H, t, *J*=6.8 Hz) ^{13}C NMR was unable to be performed due to poor solubility at concentrations required for ^{13}C NMR measurements. $[M+H]^+$: Calcd 1417.0 Found 1418.1.

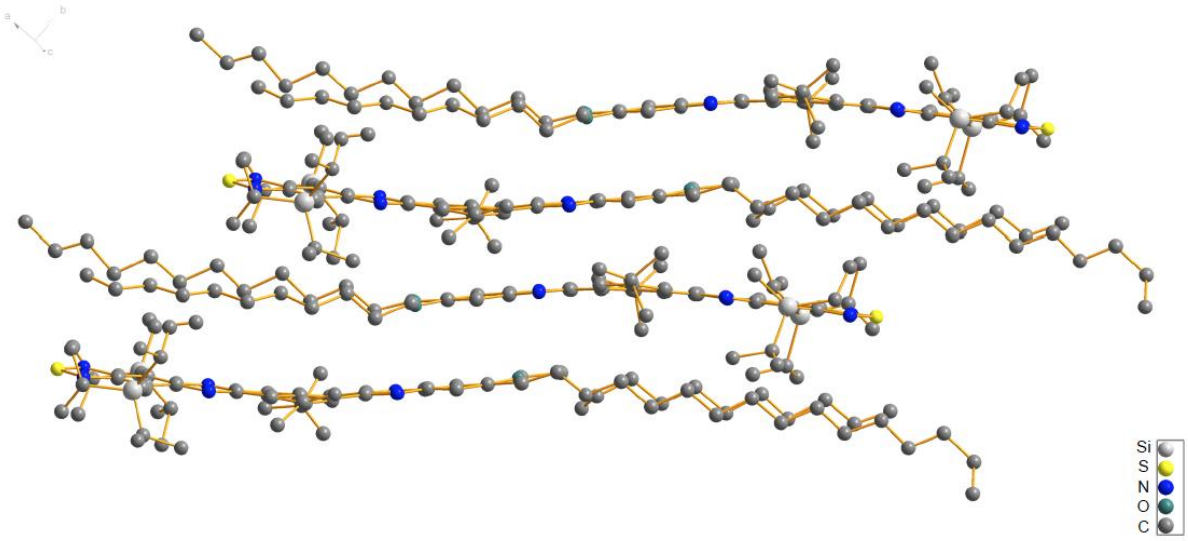


Figure S1. A partial crystal structure of compound **9**.

Table S1. Summary of Gelation Properties.[a]

Solvent	Compound **2**	Compound **4**	Compound **5**	Compound **8**
Cyclohexane	S	G (10mM, 45 ^{o}C)	G (4mM, 37 ^{o}C)	NS
Hexane	S	ppt	ppt	NS
Decane	ppt	ppt	ppt	NS
Toluene	S	S	S	ppt
Ethyl acetate	ppt	ppt	ppt	ppt
THF	S	S	S	ppt
TCE	S	S	G (26mM, 34 ^{o}C)	ppt
DCE	S	ppt	ppt	ppt
Methanol	NS	NS	NS	NS
Ethanol	NS	NS	NS	NS
Propanol	ppt	ppt	ppt	NS
CH_3CN	ppt	NS	NS	ppt
$CHCl_3$	S	S	S	PG
$CDCl_3$	S	S	S	PG
CCl4	S	S	S	ppt

[a]Abbreviations: G, gel; PG, partial gel; ppt, precipitation upon cooling; S, soluble after cooling; NS, not soluble. Critical Gel Concentration (CGC) and T_{gel} are shown in parentheses.

References:

1. D.-C. Lee, K. Jang, K. K. McGrath, R. Uy, K. A. Robins and D. W. Hatchett, *Chem. Mater.*, 2008, **20**, 3688-3695.
2. E. Perzon, X. Wang, S. Admassie, O. Inganäs and M. R. Andersson, *Polymer*, 2006, **47**, 4261-4268.