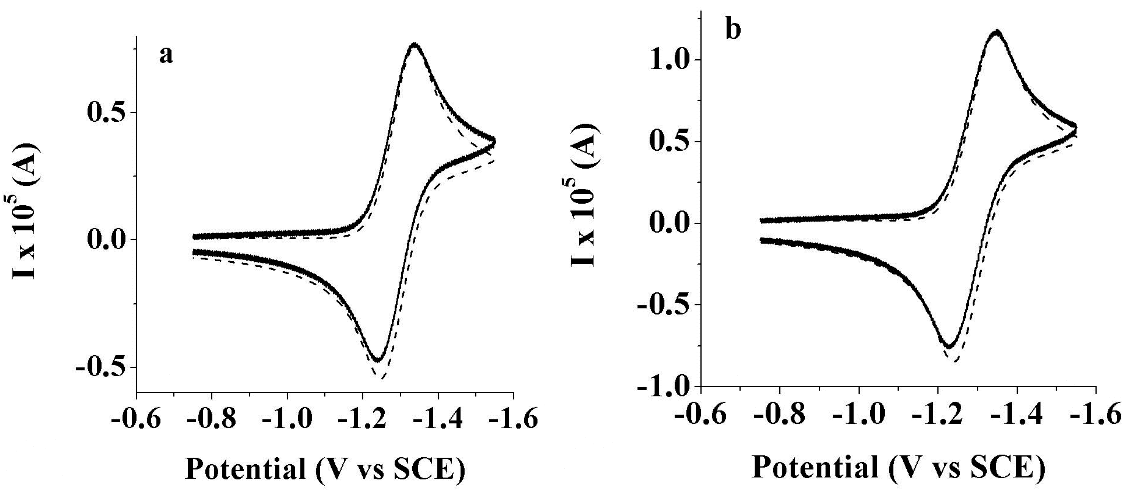
Synthesis, Photophysical, Electrochemical and Electrogenerated Chemiluminescence Studies. Multiple Sequential Electron Transfers in BODIPY Monomers, Dimers, Trimers and Polymer.

Supporting Information

Alexander B. Nepomnyashchii[γ], Martin Bröring[ƒ], Johannes Ahrens[ƒ], Allen J. Bard[γ,*]

[γ]*Center for Electrochemistry, Chemistry and Biochemistry Department, The University of Texas at Austin, Austin, Texas, 78712*

[ƒ]*Institut für Anorganische und Analytische Chemie, Technische Universität Carolo-Wilhelmina, Hagenring 30, 38106 Braunschweig, Germany*



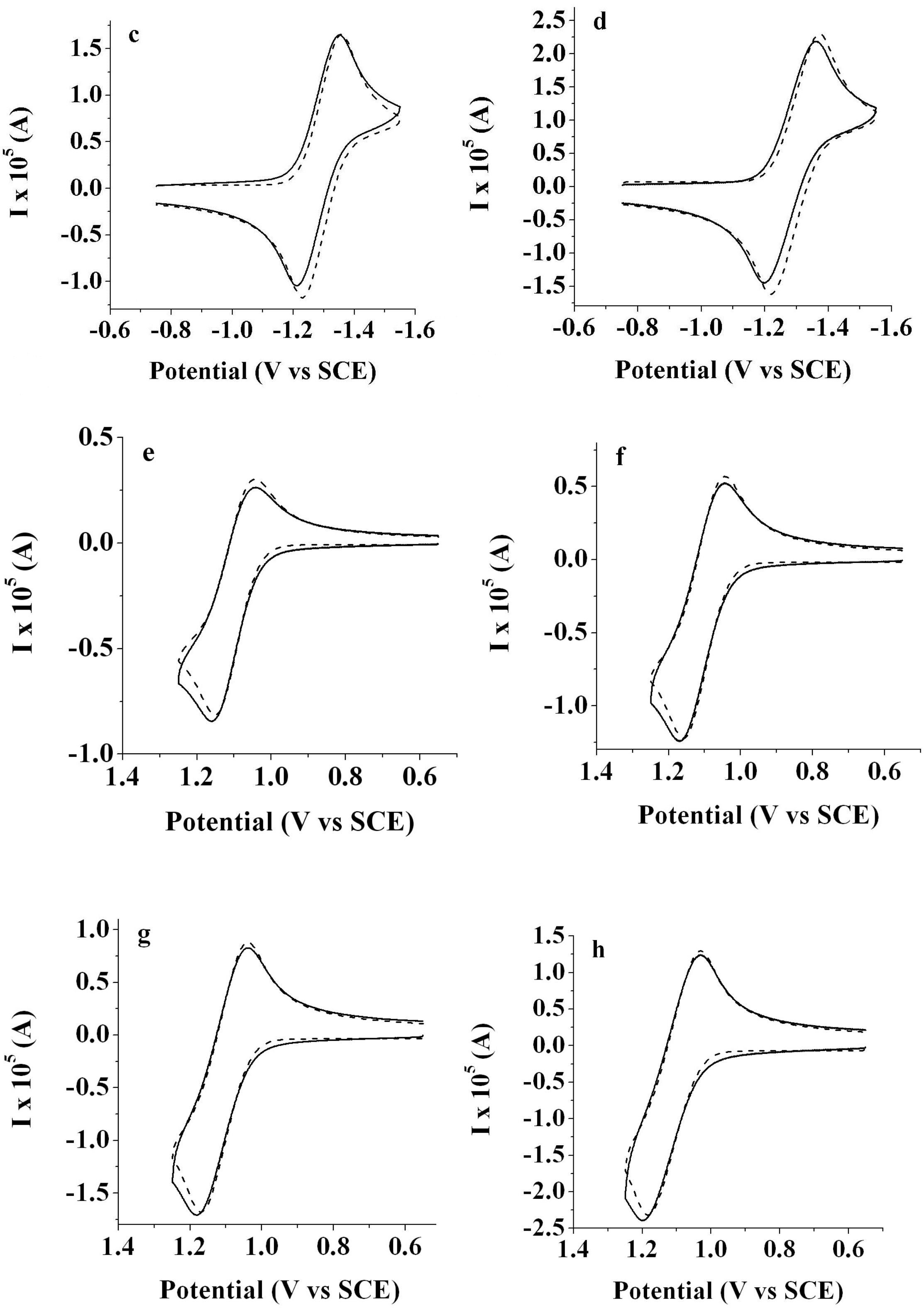
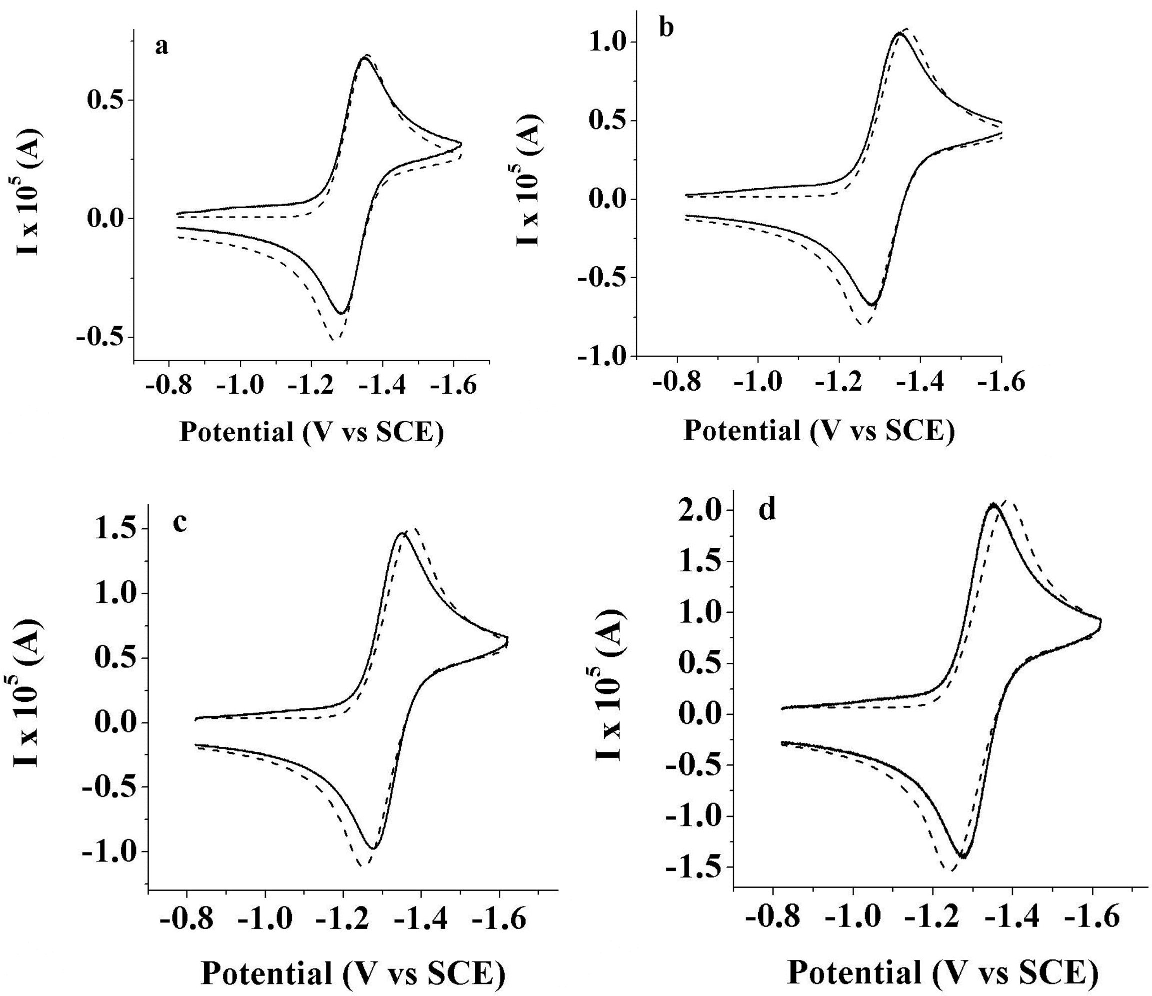
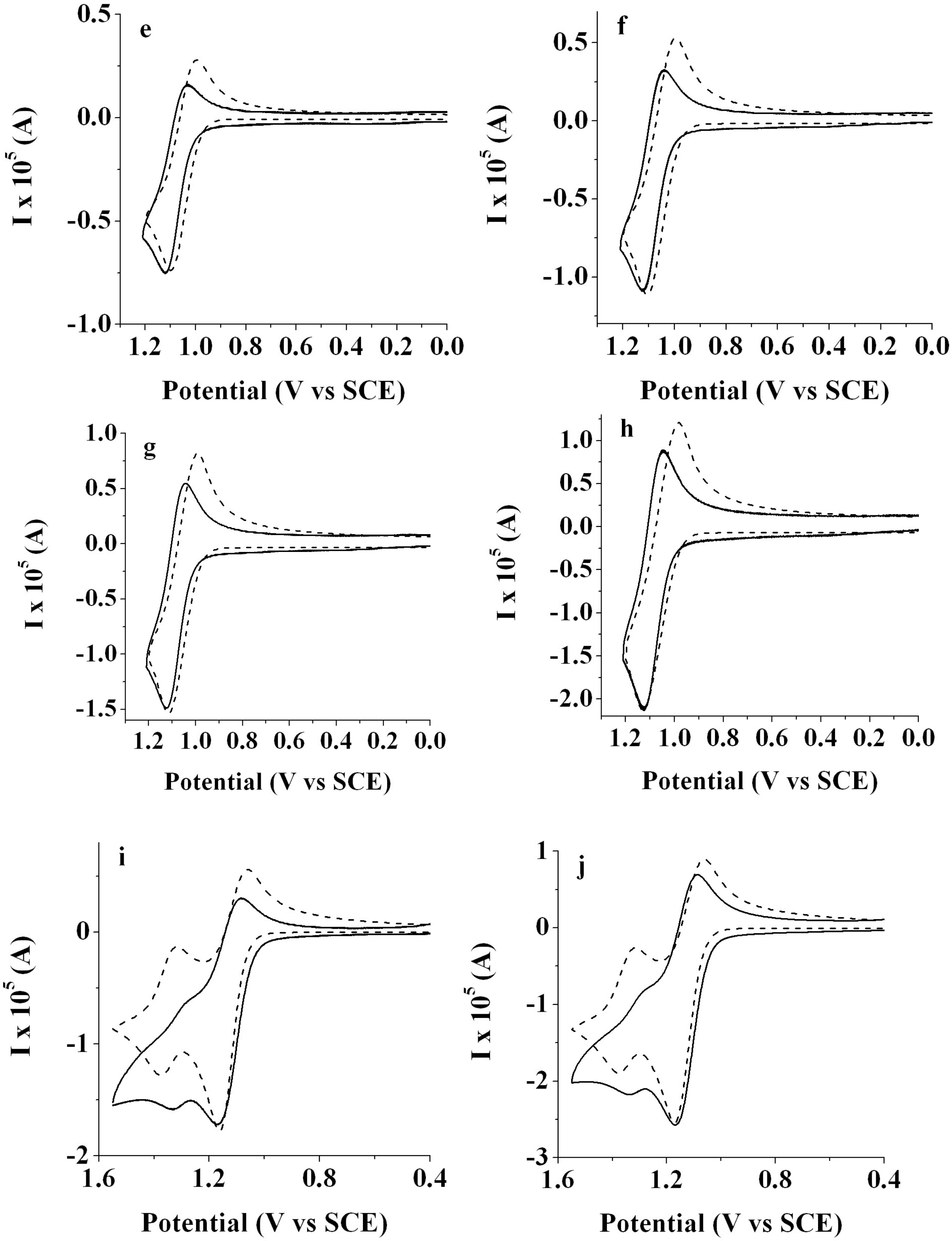

c
I x 10^5 (A)
1.5
1.0
0.5
0.0
-0.5
-1.0
-0.6 -0.8 -1.0 -1.2 -1.4 -1.6
Potential (V vs SCE)
d
I x 10^5 (A)
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-0.6 -0.8 -1.0 -1.2 -1.4 -1.6
Potential (V vs SCE)
e
I x 10^5 (A)
0.5
0.0
-0.5
-1.0
1.4 1.2 1.0 0.8 0.6
Potential (V vs SCE)
f
I x 10^5 (A)
0.5
0.0
-0.5
-1.0
1.4 1.2 1.0 0.8 0.6
Potential (V vs SCE)
g
I x 10^5 (A)
1.0
0.5
0.0
-0.5
-1.0
-1.5
1.4 1.2 1.0 0.8 0.6
Potential (V vs SCE)
h
I x 10^5 (A)
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
1.4 1.2 1.0 0.8 0.6
Potential (V vs SCE)

Figure S1. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 1.1 mM **monomer 1** during the scan in the negative direction (a)-(d) and positive direction (e)-(h). Scan rate (a) and (e) 0.1 V/s; (b) and (f) 0.25 V/s; (c) and (g) 0.5 V/s; (e) and (h) 1 V/s. Experimental data: solvent: DCM; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area 0.0314 cm^2. Simulated data: $E_{1/2}^{1}$ =1.12 V; $E_{1/2}^{2}$ = 1.31 V; $E_{1/2}^{d}$= 1.09 V; k_{dim} = 400 M^{-1} s^{-1} and k = 10^{10} s^{-1}; diffusion coefficient for the monomer 7.0 x 10^{-6} cm^2/s and dimer 5.2 x 10^{-6} cm^2/s; uncompensated resistance 1800 Ω; capacitance 7 x 10^{-7} F.




e
f
g
h
i
j
I x 10^5 (A)
Potential (V vs SCE)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
1.0
1
0
-1
-2
-3
1.6
1.2
1.0
0.8
0.6
0.4
0.2
0.0

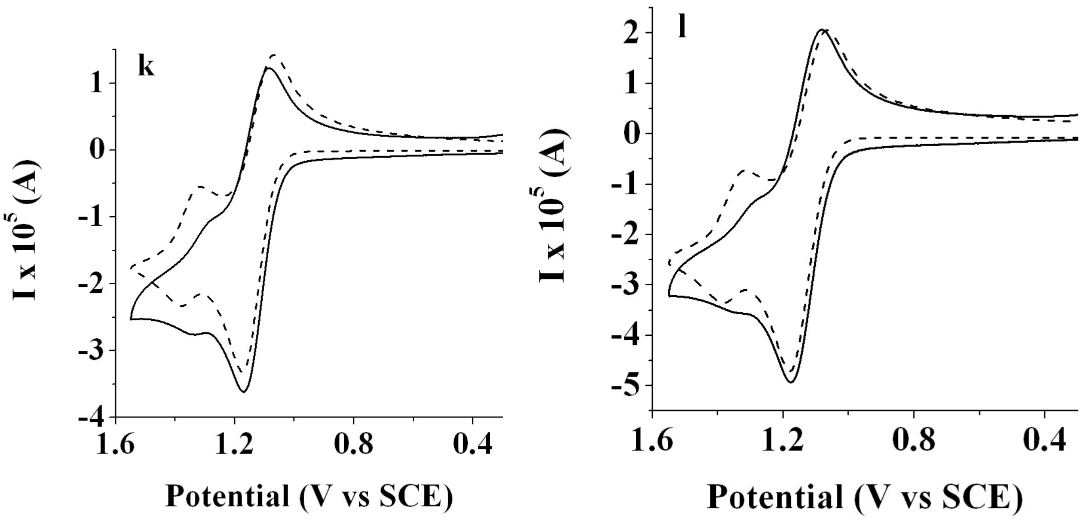
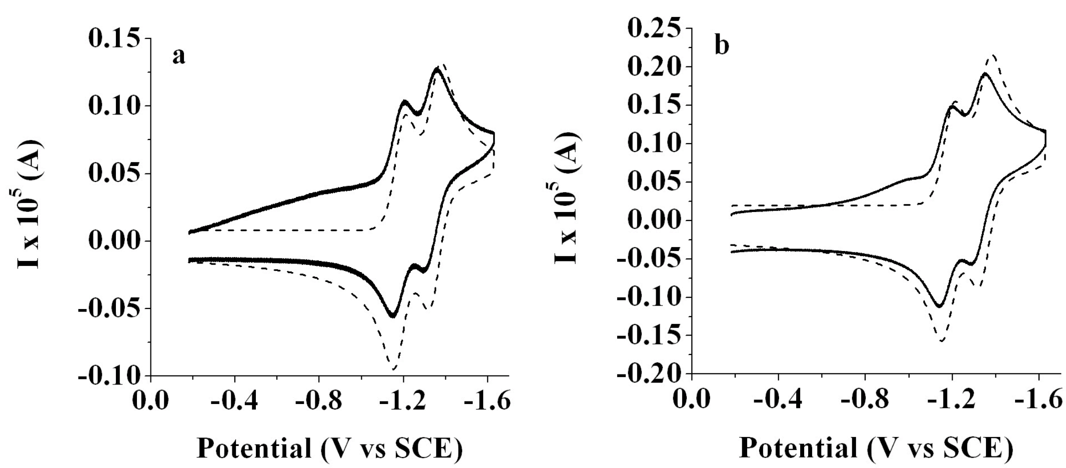


Figure S2. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 1.0 mM **monomer 2** during the scan in the negative direction (a)-(d) and positive direction (e)-(h) and (i)-(l) 2.3 mM monomer 2. Scan rate (a), (e) and (i) 0.1 V/s; (b) and (f) and (j) 0.25 V/s; (c), (g) and (k) 0.5 V/s; (e), (h) and (l) 1 V/s. Experimental data: solvent: DCM; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area 0.0314 cm^2. Simulated data: $E_{1/2}^{1}$ =1.14 V; $E_{1/2}^{2}$ = 1.36 V; $E_{1/2}^{d}$= 1.10 V; k_{dim} = 2000 M^{-1} s^{-1} and k = 10^{10} s^{-1}; diffusion coefficient for the monomer 7.0 x 10^{-6} cm^2/s and dimer 5.2 x 10^{-6} cm^2/s; uncompensated resistance 300 Ω; capacitance 8 x 10^{-7} F.



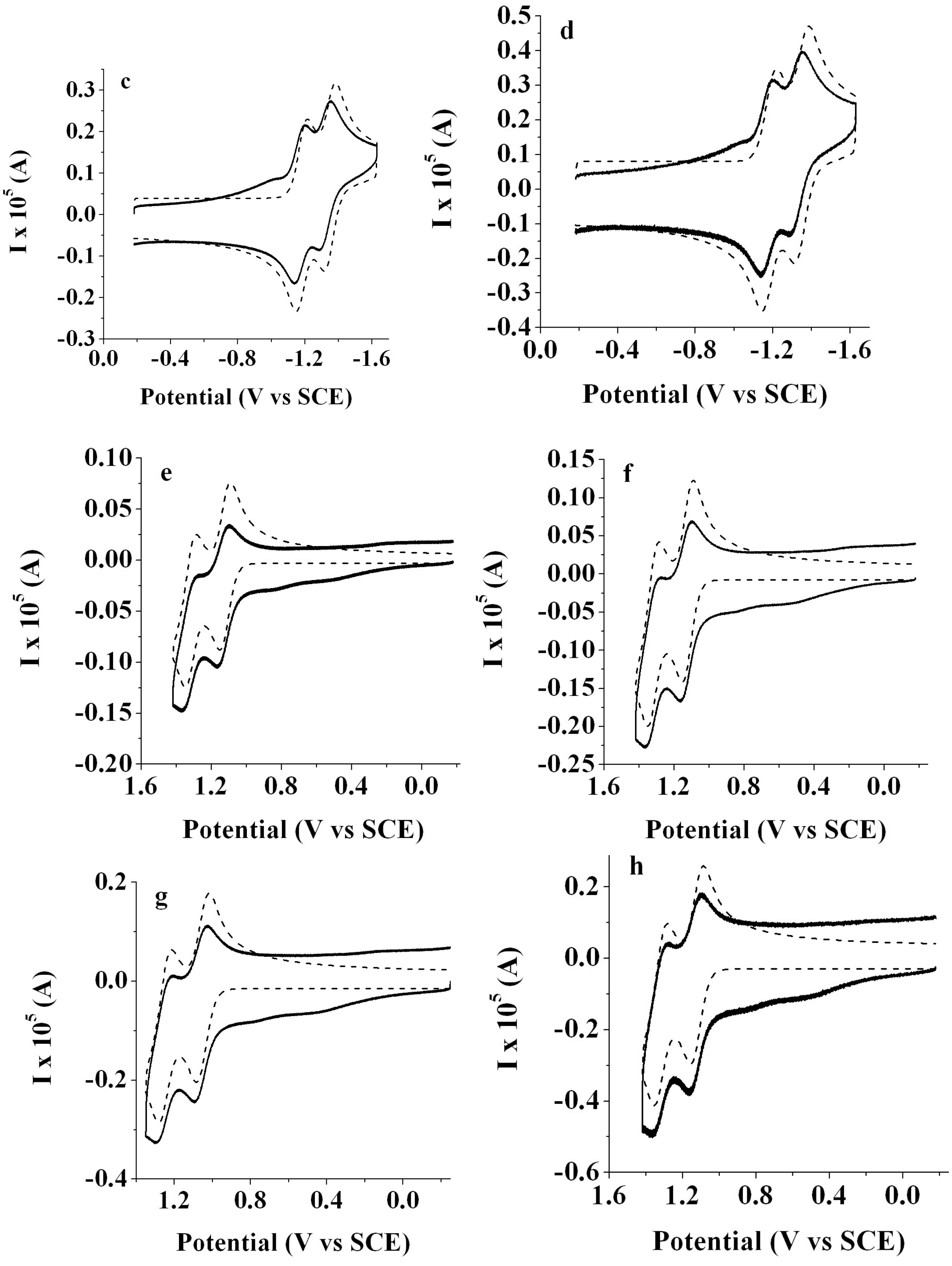
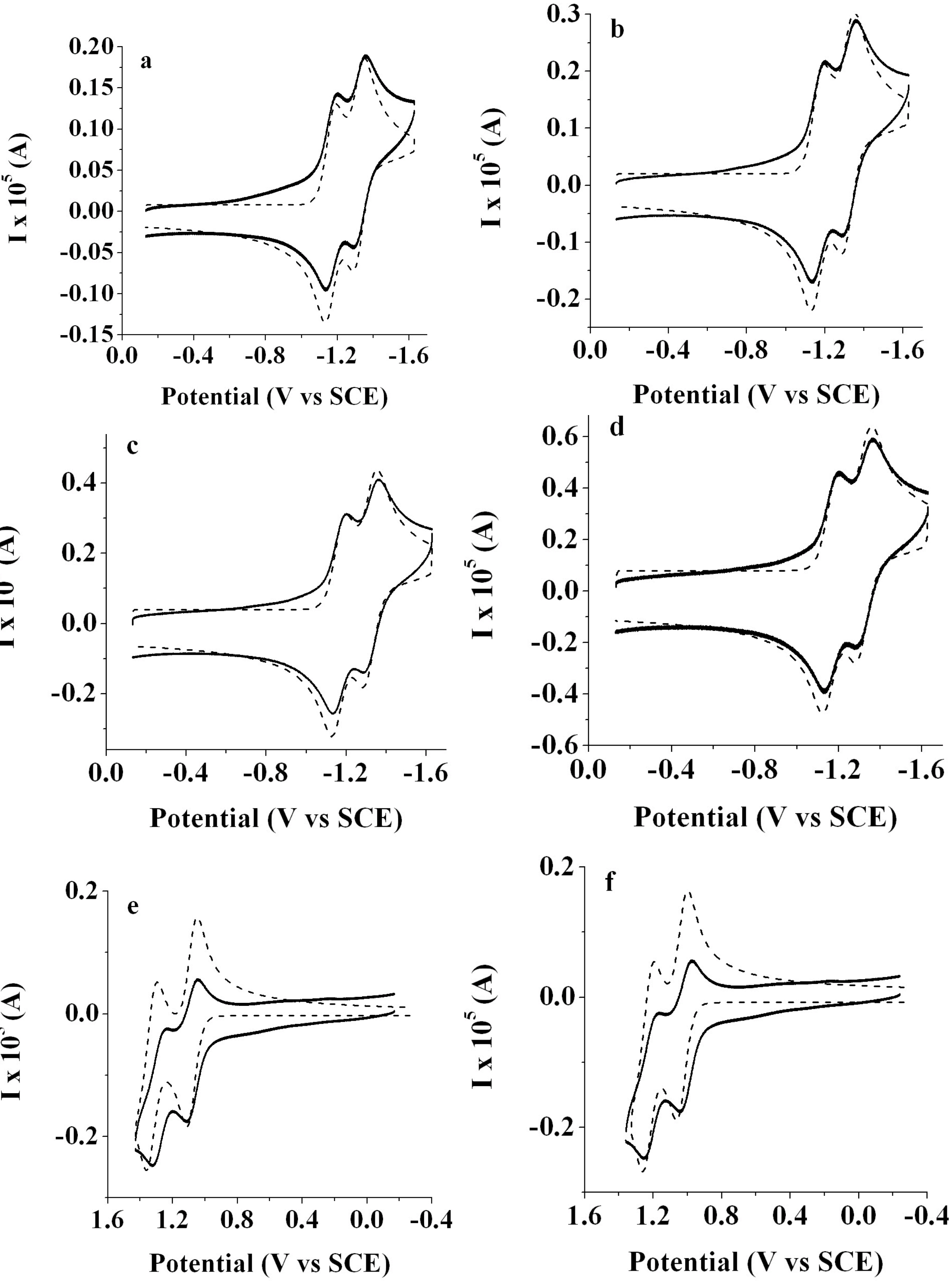


Figure S3. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.14 mM **dimer 1** during the scan in the negative direction (a)-(d) and positive direction (e)-(h). Scan rate (a) and (e) 0.1 V/s; (b) and (f) 0.25 V/s; (c) and (g) 0.5 V/s; (e) and (h) 1 V/s. Experimental data: solvent: DCM; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area 0.0314 cm^2. Simulated data: diffusion coefficient: 5.2 x 10^{-6} cm^2/s; uncompensated resistance 1800 Ω; capacitance 3 x 10^{-7} F.



a
b
c
d
e
f
I x 10^5 (A)
Potential (V vs SCE)
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
0.3
0.2
0.1
0.0
-0.1
-0.2
0.6
0.4
-0.4
-0.6
0.0
-0.4
-0.8
-1.2
-1.6
1.6
1.2
0.8
0.4

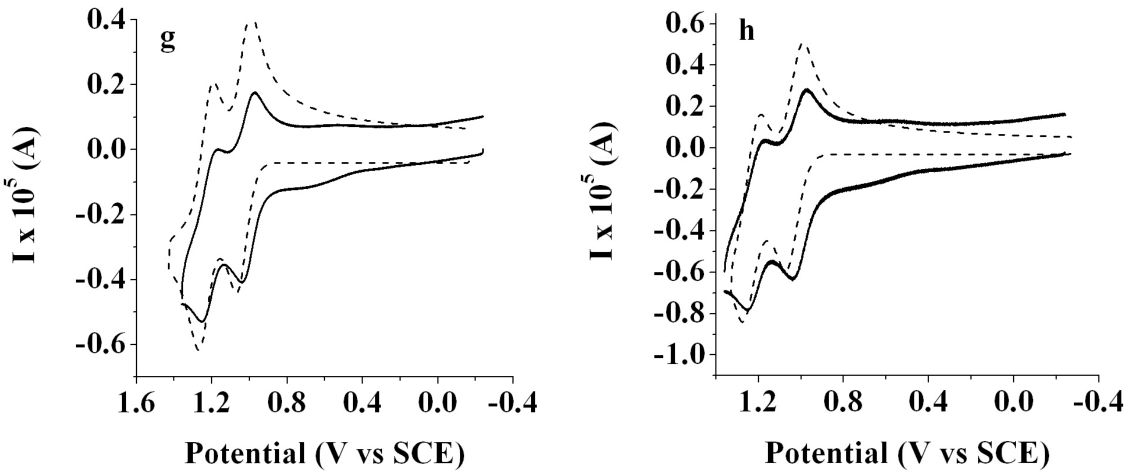
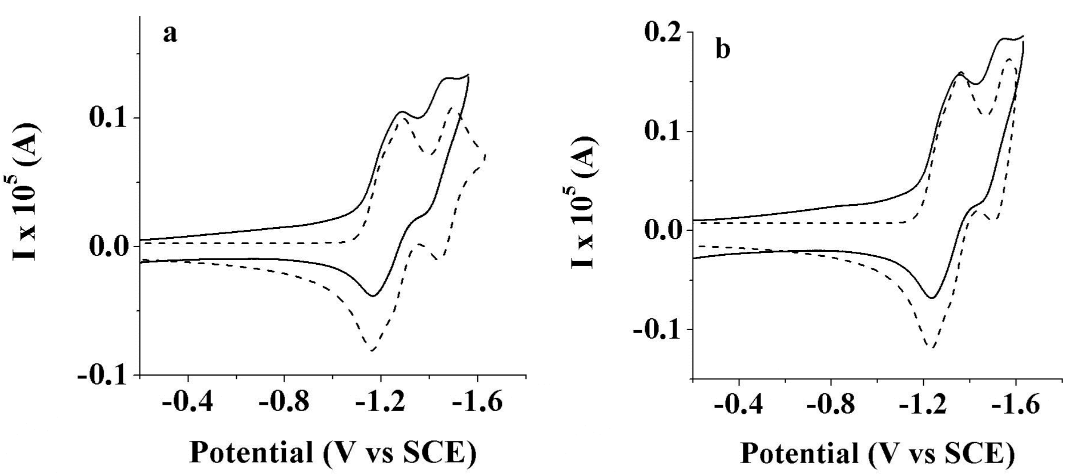


Figure S4. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.2 mM **dimer 2** during the scan in the negative direction (a)-(d) and positive direction (e)-(h). Scan rate (a) and (e) 0.1 V/s; (b) and (f) 0.25 V/s; (c) and (g) 0.5 V/s; (e) and (h) 1 V/s. Experimental data: solvent: DCM; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area 0.0314 cm^2. Simulated data: diffusion coefficient: 5.2 x 10^{-6} cm^2/s; uncompensated resistance 1800 Ω; capacitance 8 x 10^{-7} F.



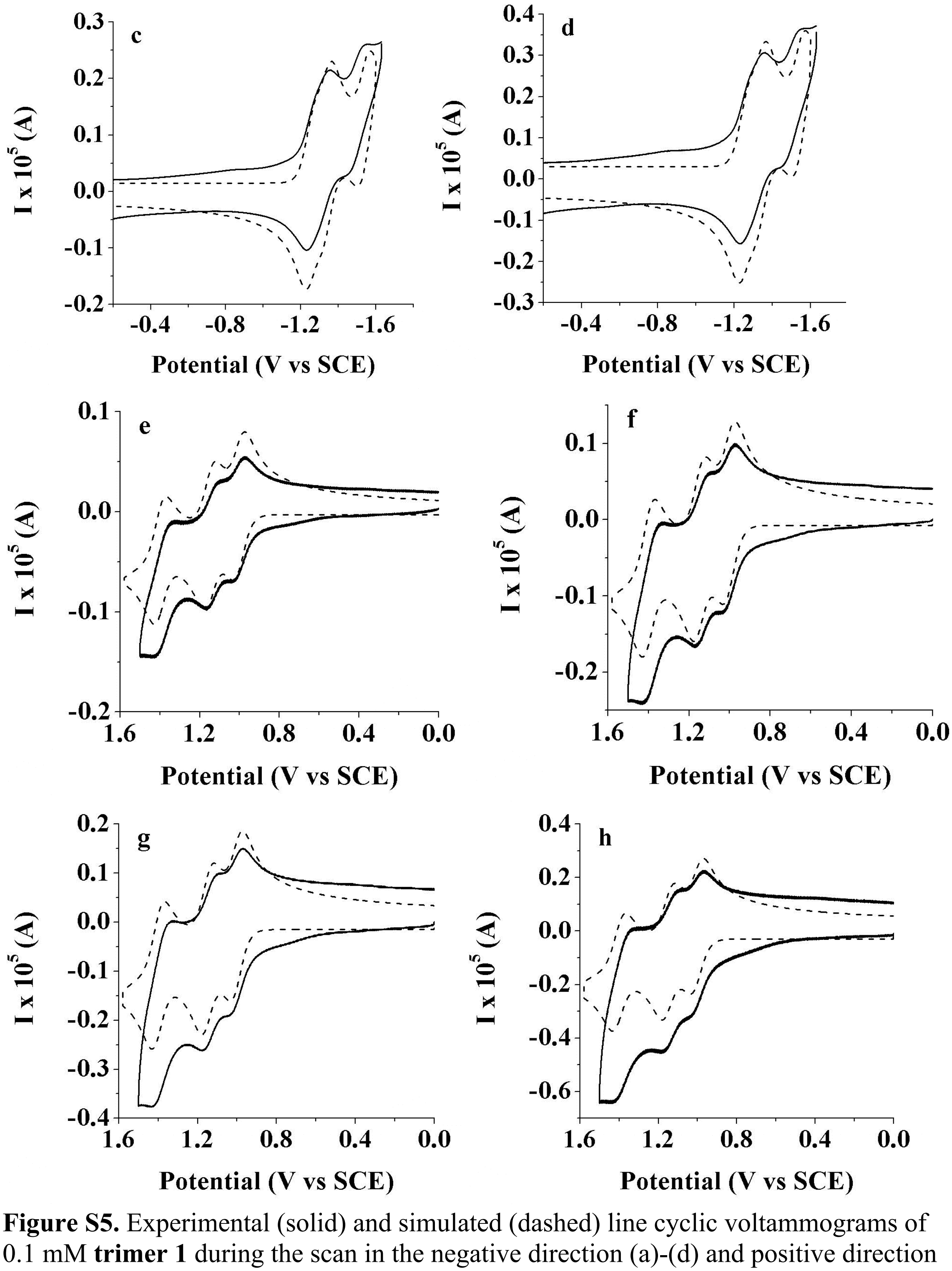
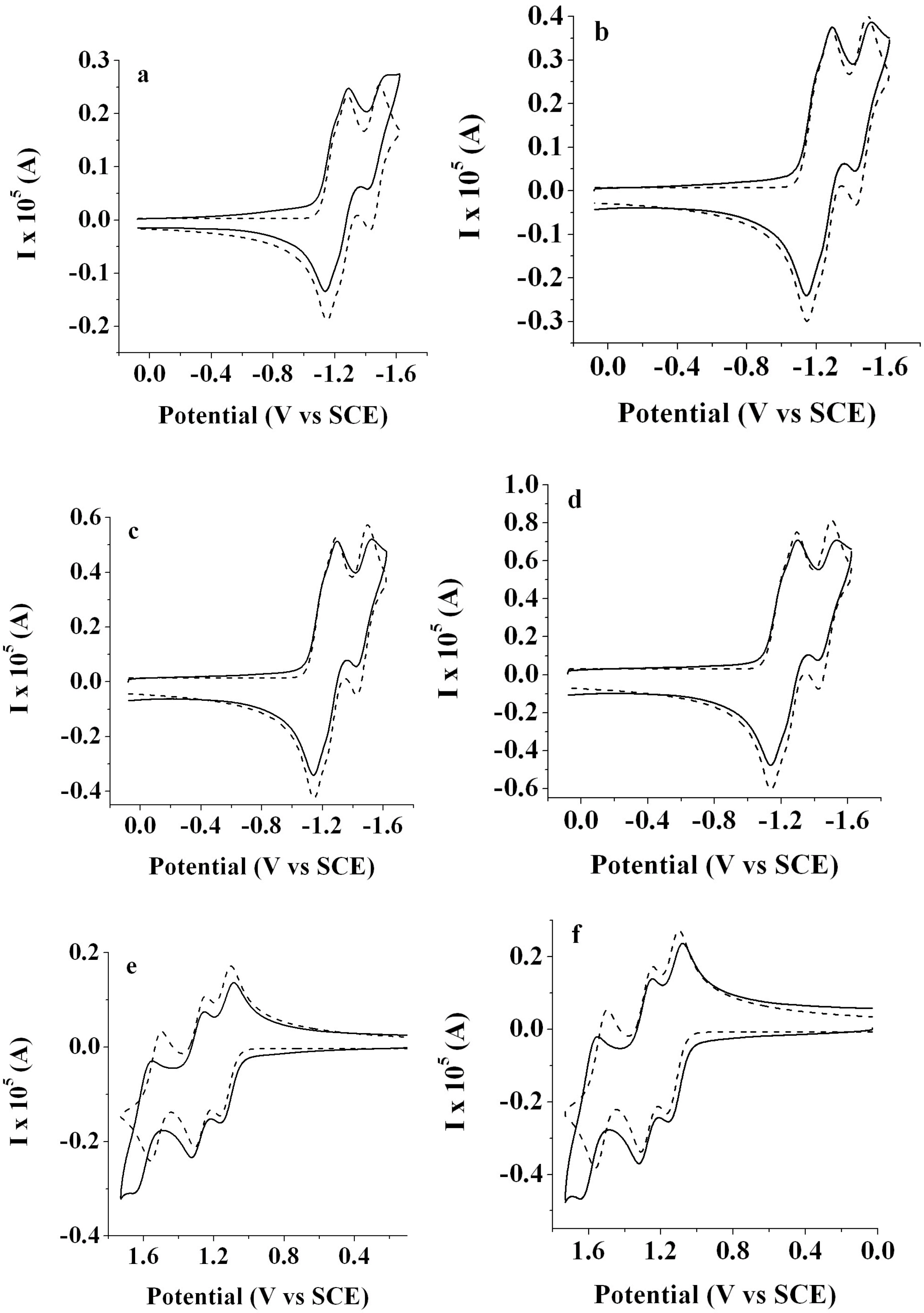


Figure S5. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.1 mM **trimer 1** during the scan in the negative direction (a)-(d) and positive direction (e)-(h). Scan rate (a) and (e) 0.1 V/s; (b) and (f) 0.25 V/s; (c) and (g) 0.5 V/s; (e) and (h) 1 V/s. Experimental data: solvent: DCM; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area 0.0314 cm^2. Simulated data: diffusion coefficient: 4.8 x 10^{-6} cm^2/s; uncompensated resistance 1800 Ω; capacitance 3 x 10^{-7} F.


a
I x 10^5 (A)
Potential (V vs SCE)
b
I x 10^5 (A)
Potential (V vs SCE)
c
I x 10^5 (A)
Potential (V vs SCE)
d
I x 10^5 (A)
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f
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Potential (V vs SCE)

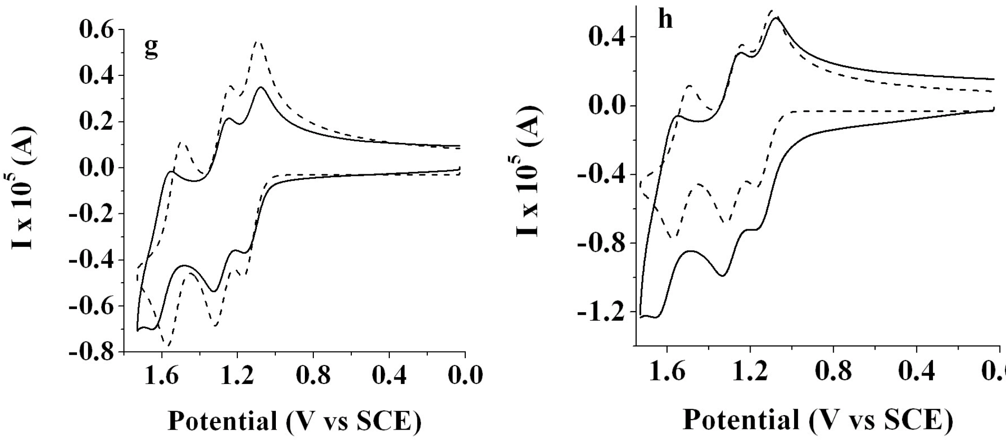
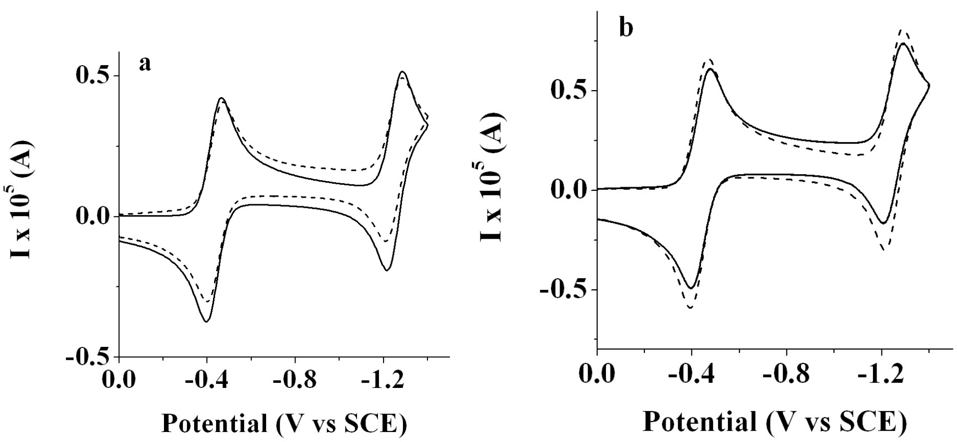


Figure S6. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.24 mM **trimer 2** during the scan in the negative direction (a)-(d) and positive direction (e)-(h). Scan rate (a) and (e) 0.1 V/s; (b) and (f) 0.25 V/s; (c) and (g) 0.5 V/s; (e) and (h) 1 V/s. Experimental data: solvent: DCM; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area 0.0314 cm^2. Simulated data: diffusion coefficient: 4.8 x 10^{-6} cm^2/s; uncompensated resistance 1800 Ω; capacitance 3 x 10^{-7} F.



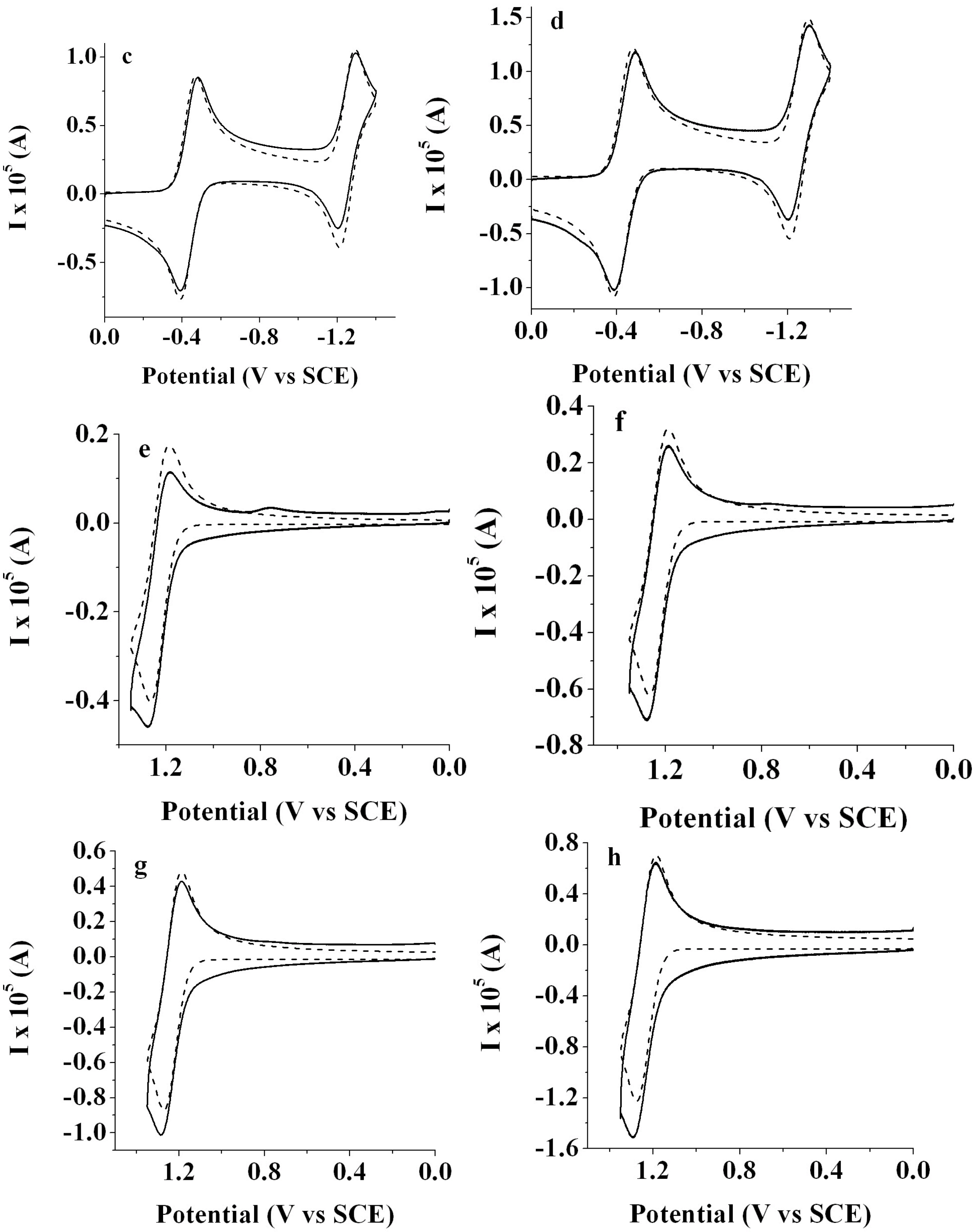
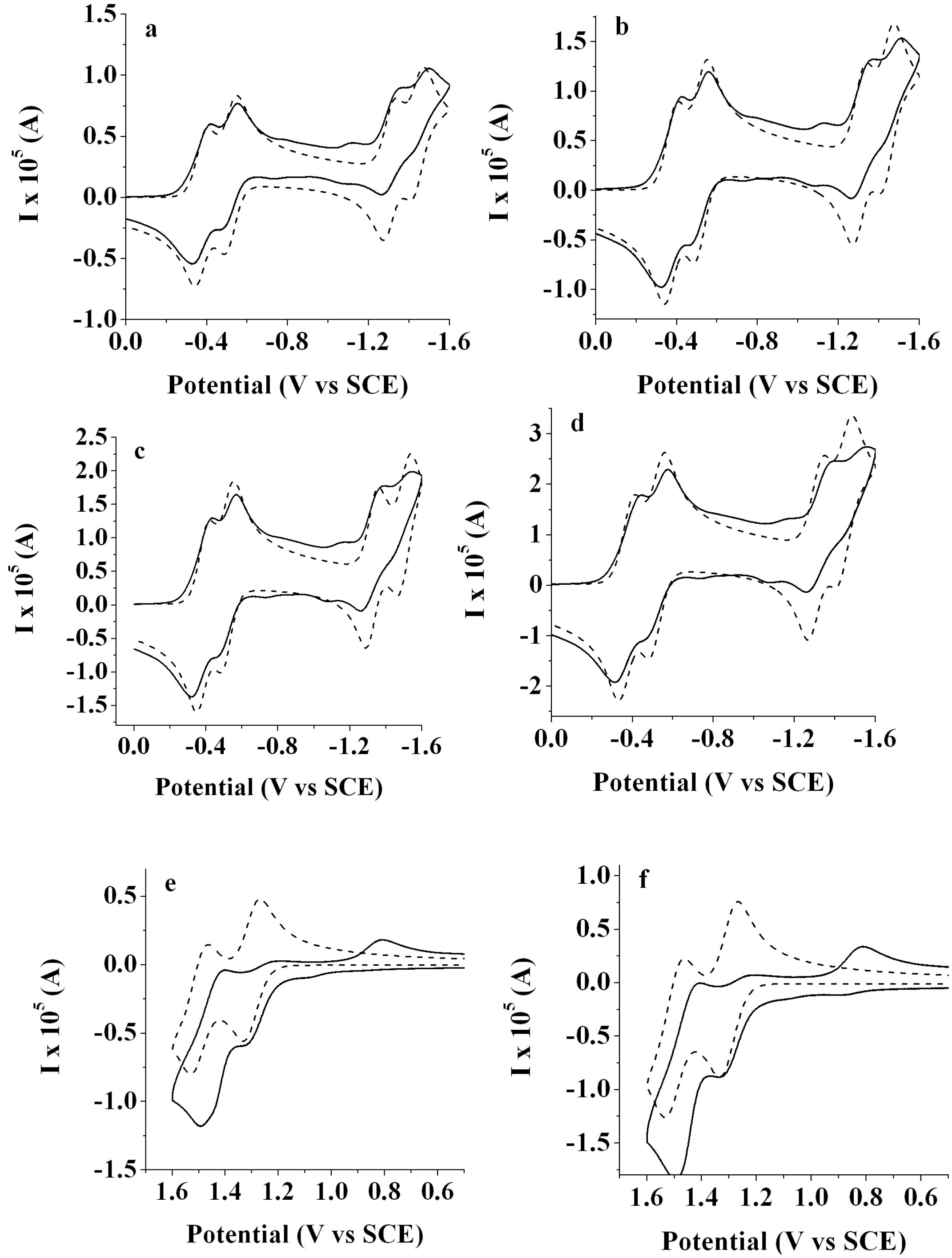


Figure S7. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.6 mM of **aza-BODIPY monomer** during (a-d) scans into the positive and (e-h) negative direction. Scan rate: (a) and (e) 0.1 V/s; (b) and (f) 0.25 V/s; (c) and (g) 0.5 V/s; (d) and (h) 1 V/s. Experimental data: solvent: DCM; supporting electrolyte: 0.1 M $TBAPF_6$; electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient of the monomer is 7.0 x 10^{-6} cm^2/s and dimer 5.2 x 10^{-6} cm^2/s; uncompensated resistance 1000 Ω, capacitance 3 x 10^{-7} F and kinetics constant of 2 s^{-1} were used in simulations for reduction and 400 M^{-1} s^{-1} dimerization constant and deprotonation constant of 10^{10} s^{-1} for oxidation. As shown, the current scale encompasses ± 5 μA.



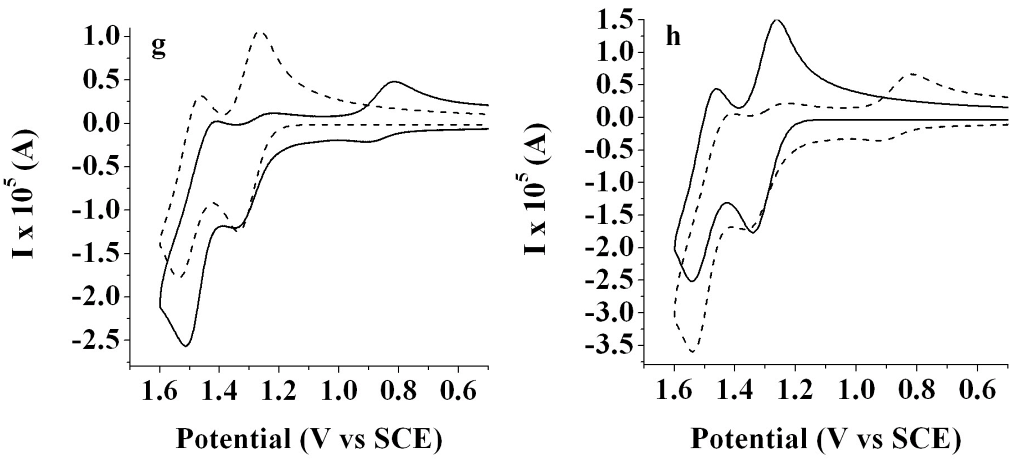
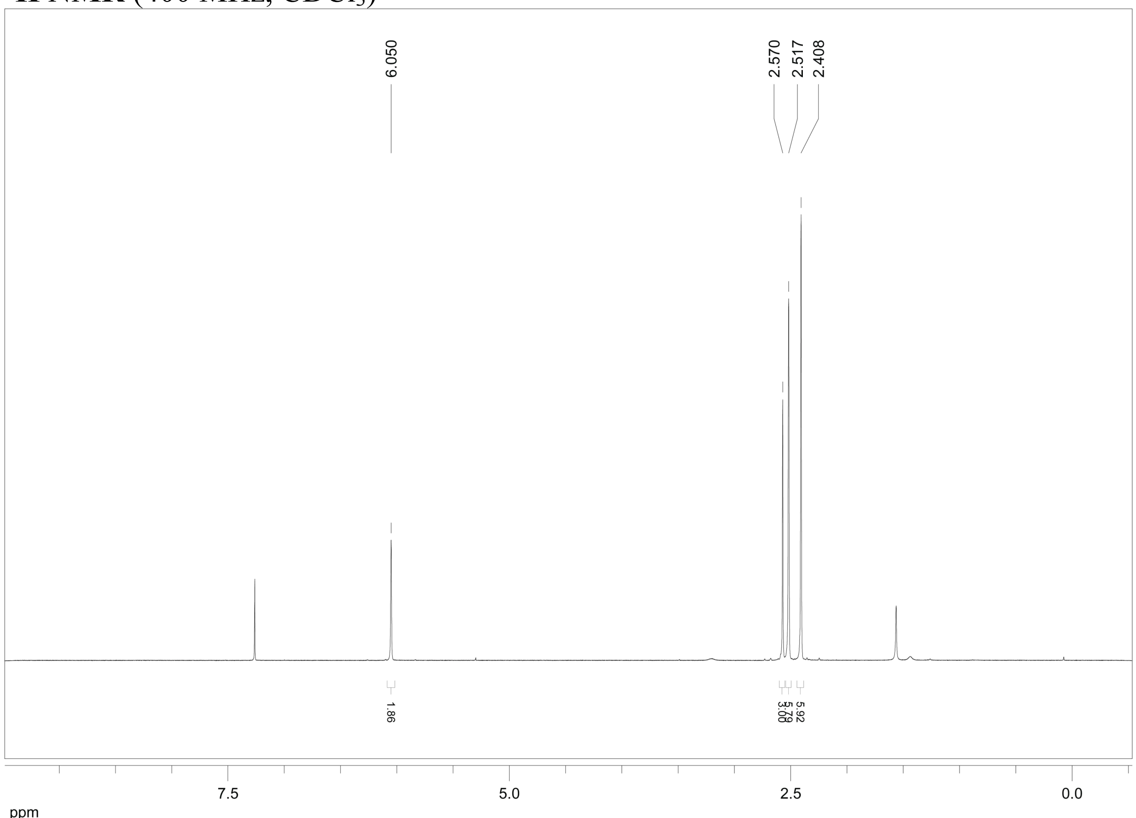


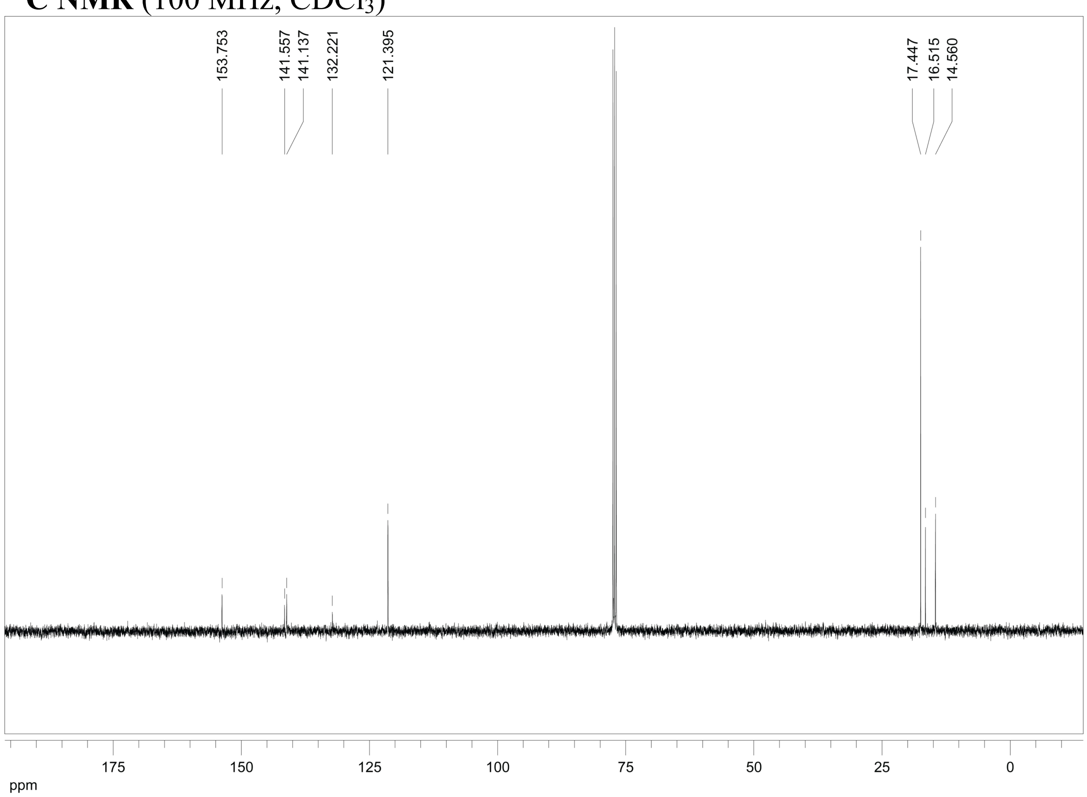
Figure S8. Experimental (solid) and simulated (dashed) cyclic voltammograms of 0.9 mM of **aza-BODIPY dimer**; Scan rate: (a) and (e) 0.1 V/s; (b) and (f) 0.25 V/s; (c) and (g) 0.5 V/s; (d) and (h) 1 V/s. Experimental data: solvent DCM; platinum electrode area 0.0314 cm^2. Simulated data: diffusion coefficient of the **aza-BODIPY dimer** 5.2 x 10^{-6} cm^2/s; uncompensated resistance: 500 Ω; capacitance 3 x 10^{-7} F.

Monomer 1

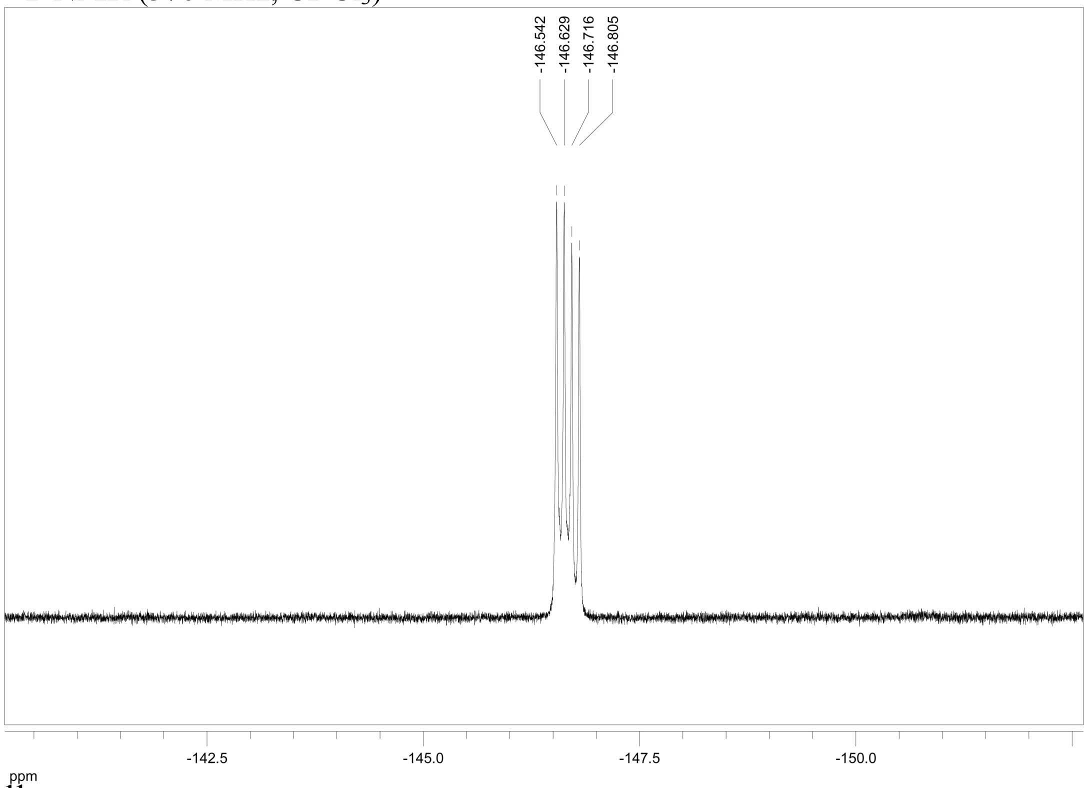
^{1}H NMR (400 MHz, $CDCl_3$)



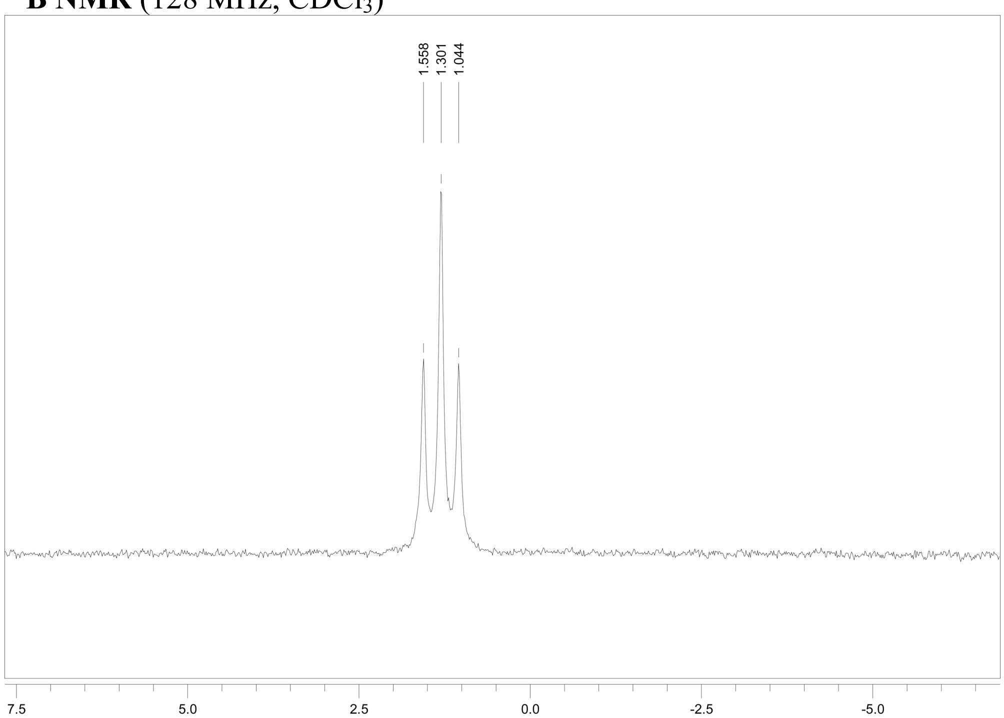
^{13}C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

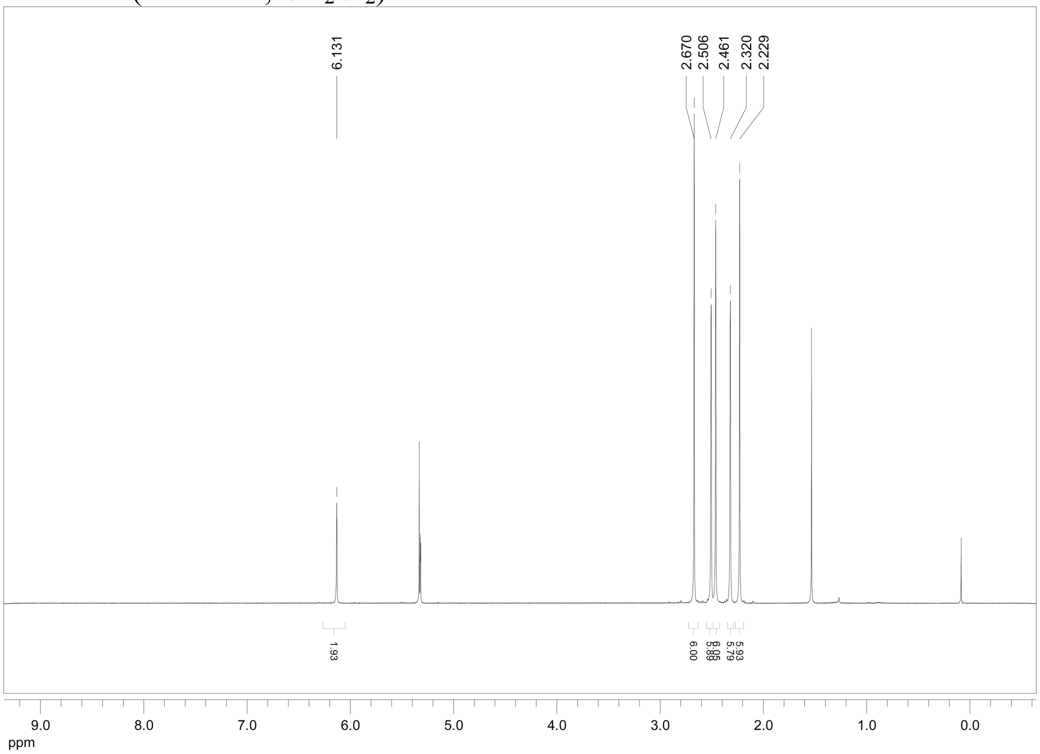


^{11}B NMR (128 MHz, $CDCl_3$)

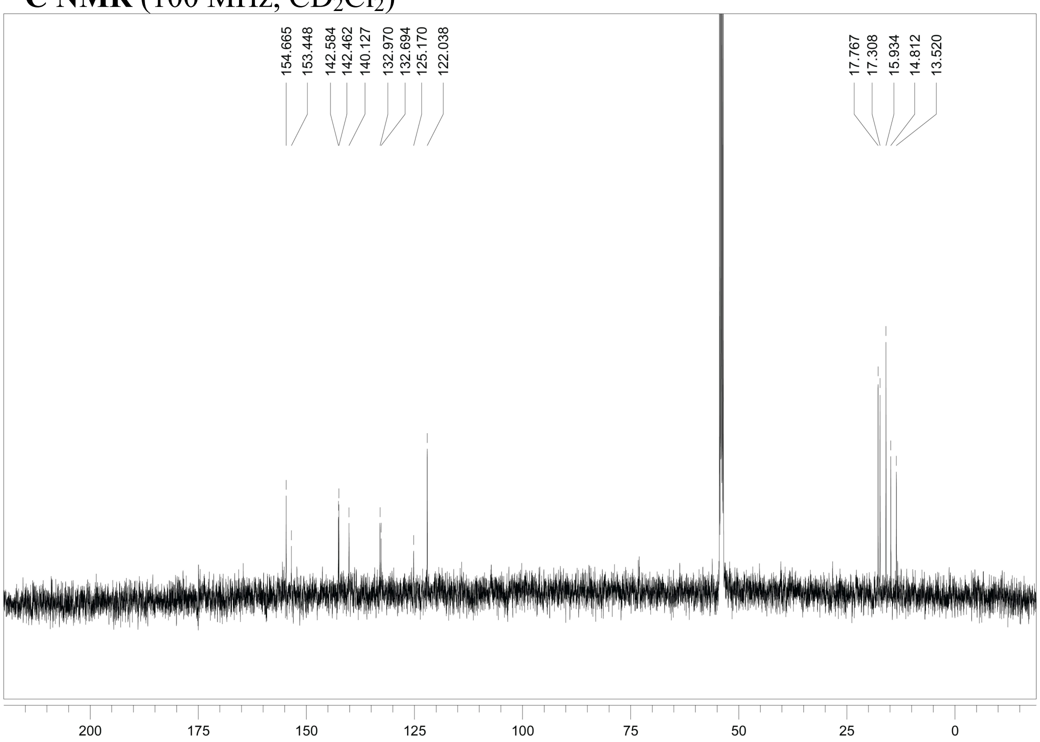


Dimer 1

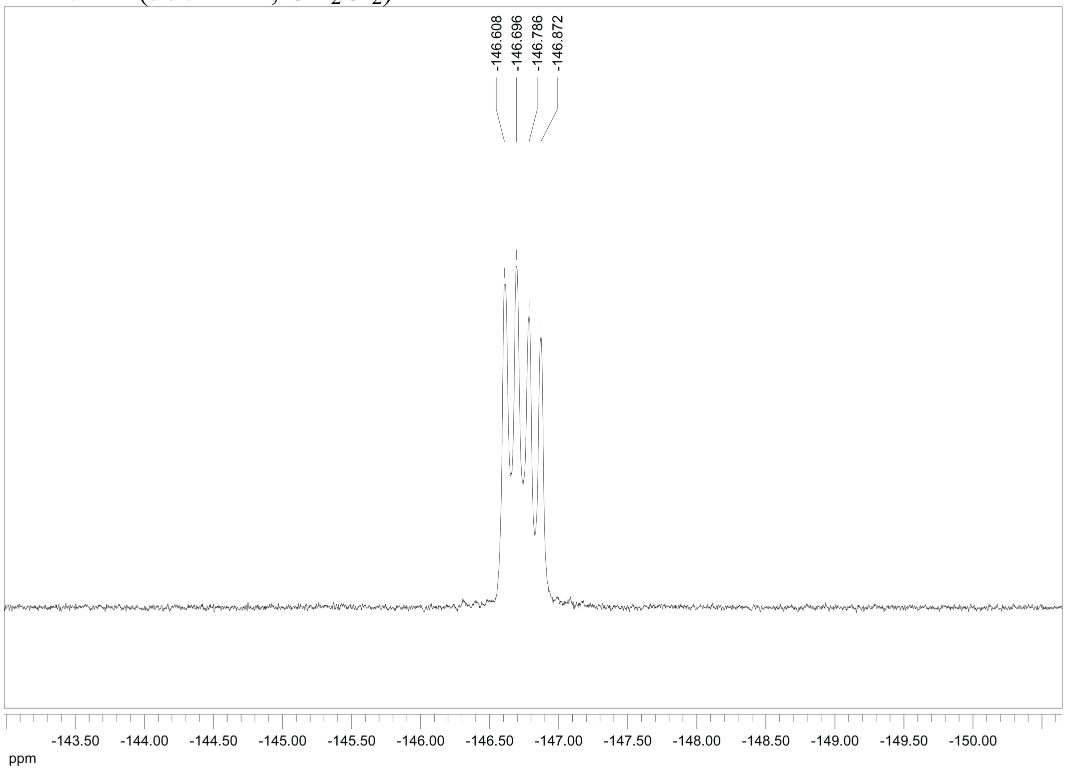
^{1}H NMR (400 MHz, CD_2Cl_2)



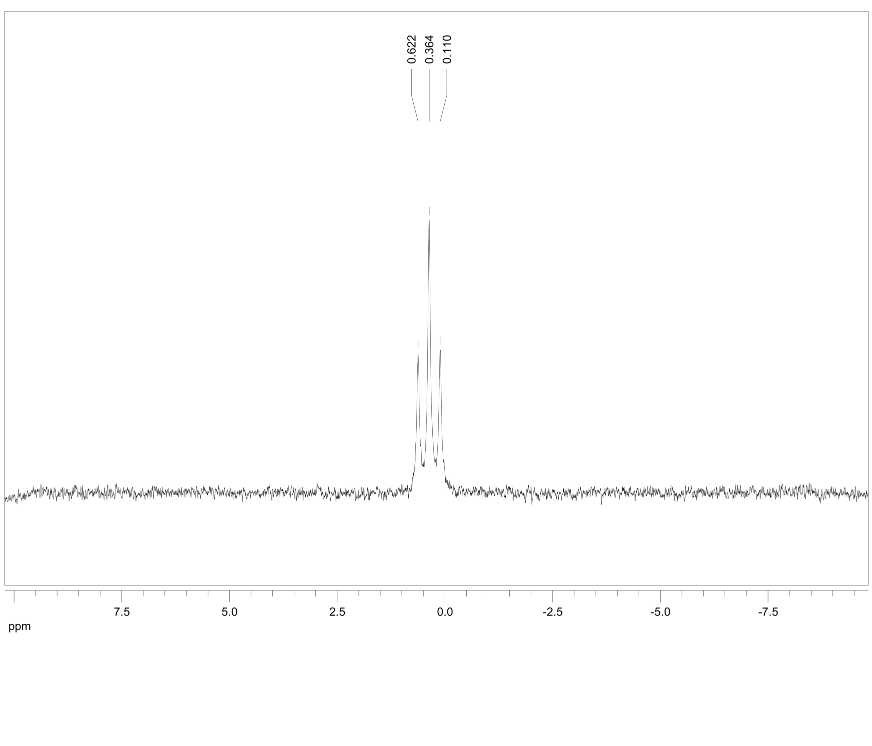
^{13}C NMR (100 MHz, CD_2Cl_2)



^{19}**F NMR** (376 MHz, CD_2Cl_2)

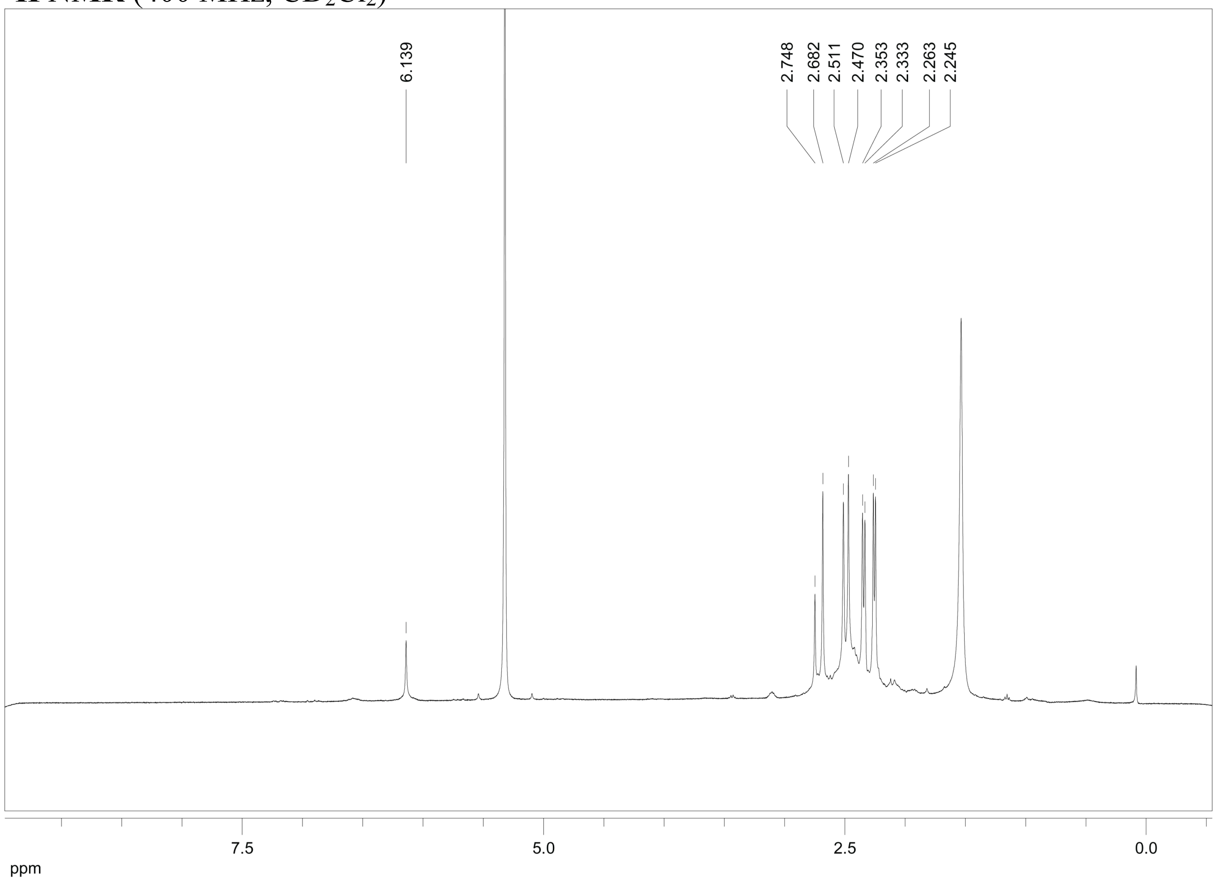


^{11}**B NMR** (128 MHz, CD_2Cl_2)

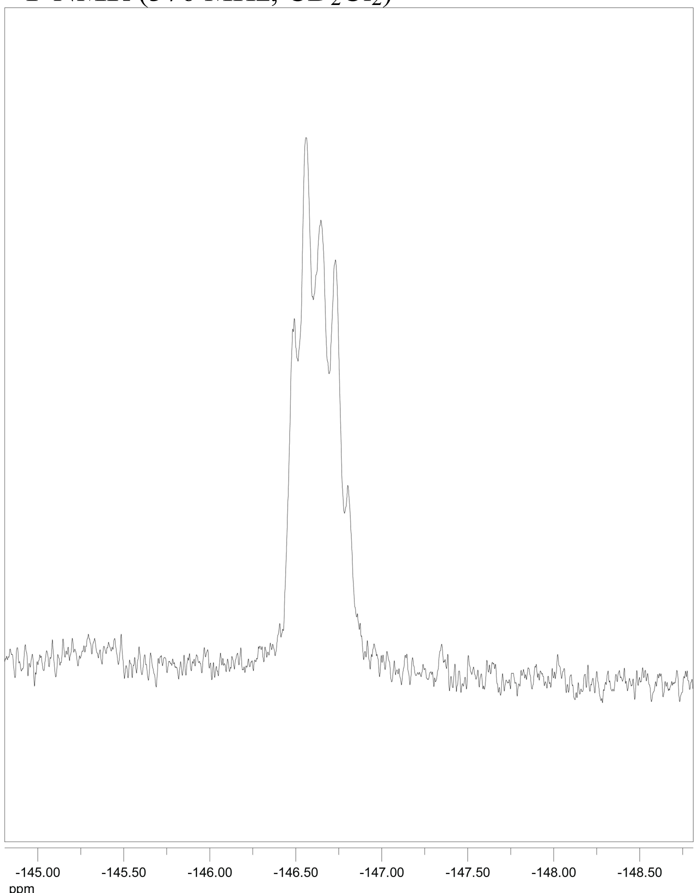


Trimer 1

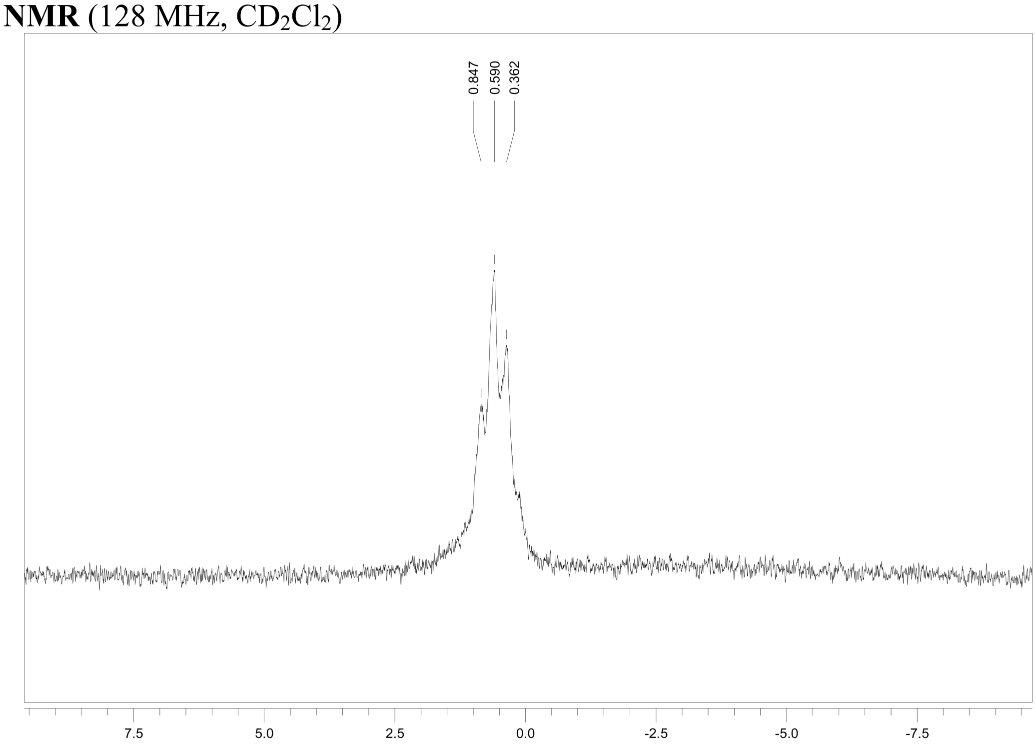
^{1}H NMR (400 MHz, CD_2Cl_2)



^{19}F NMR (376 MHz, CD_2Cl_2)

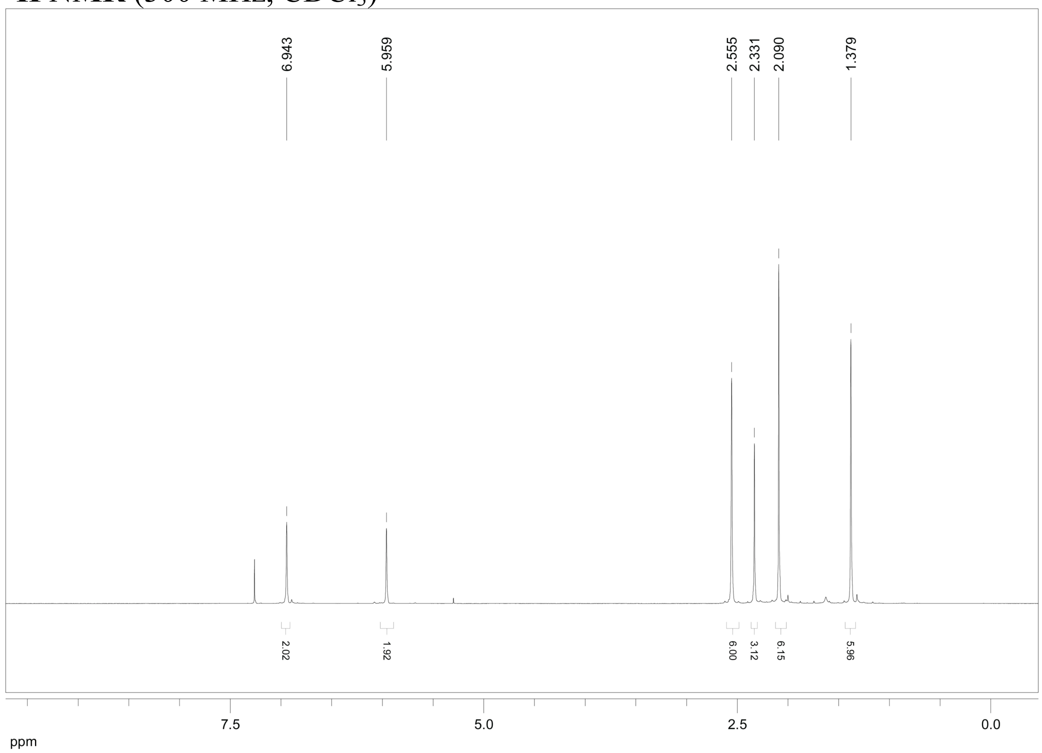


^{11}B NMR (128 MHz, CD_2Cl_2)

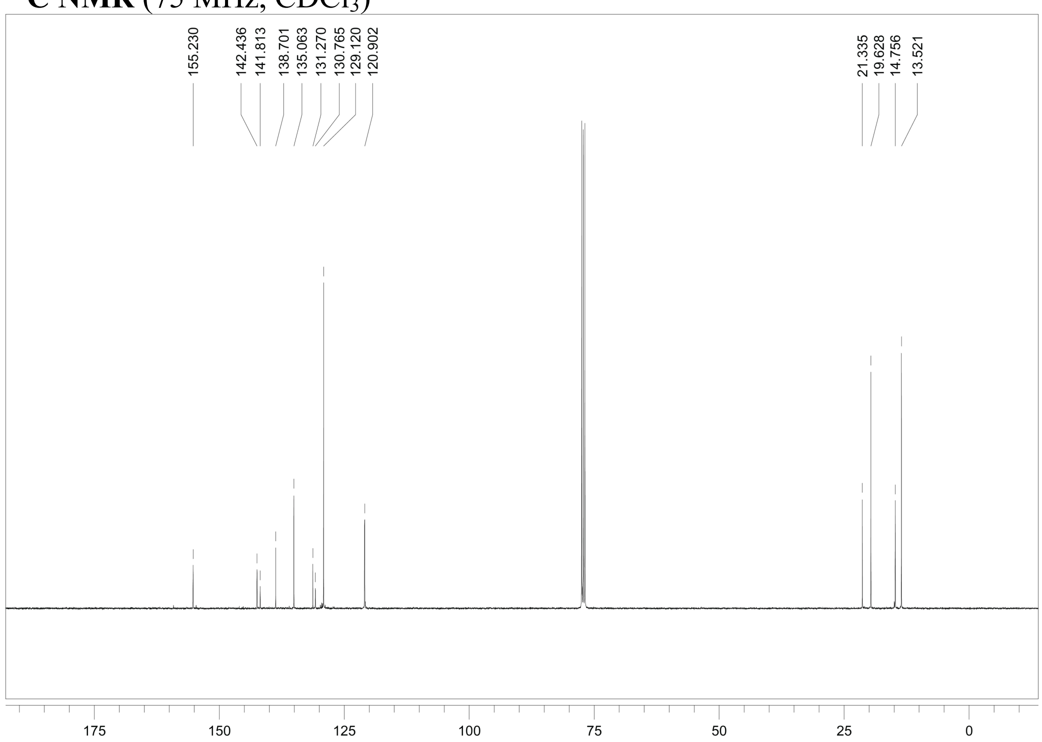


Monomer 2

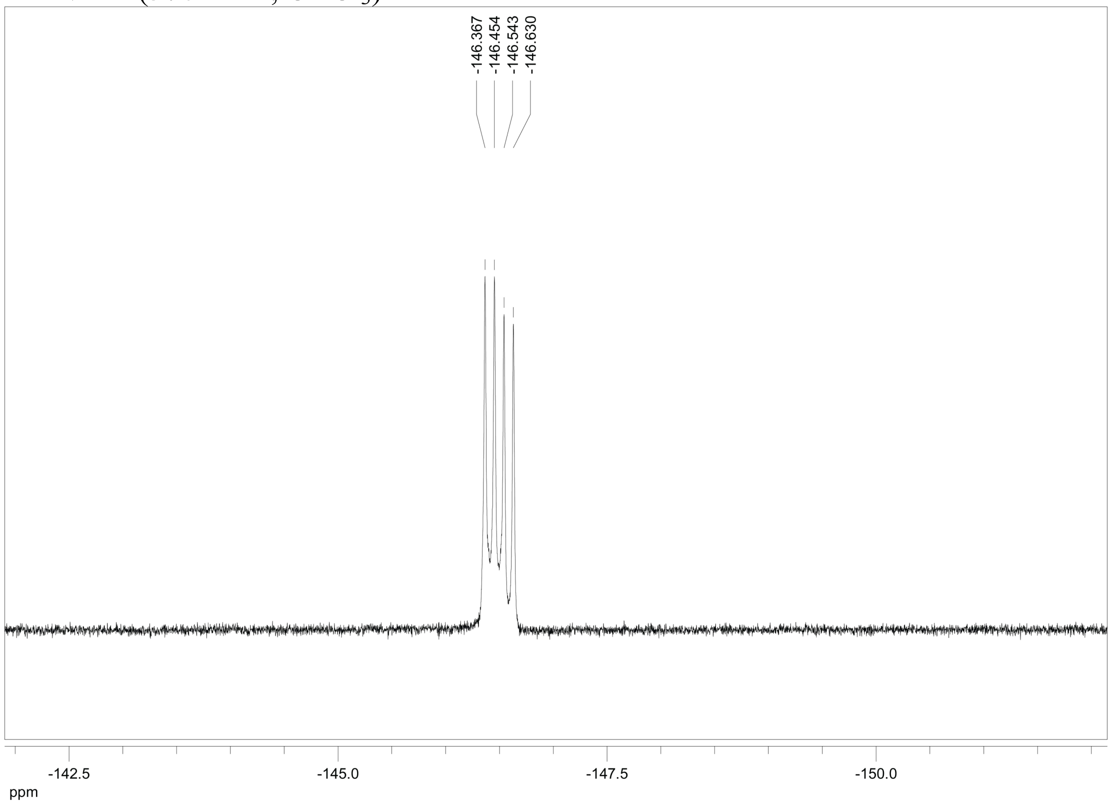
[1]H NMR (300 MHz, $CDCl_3$)



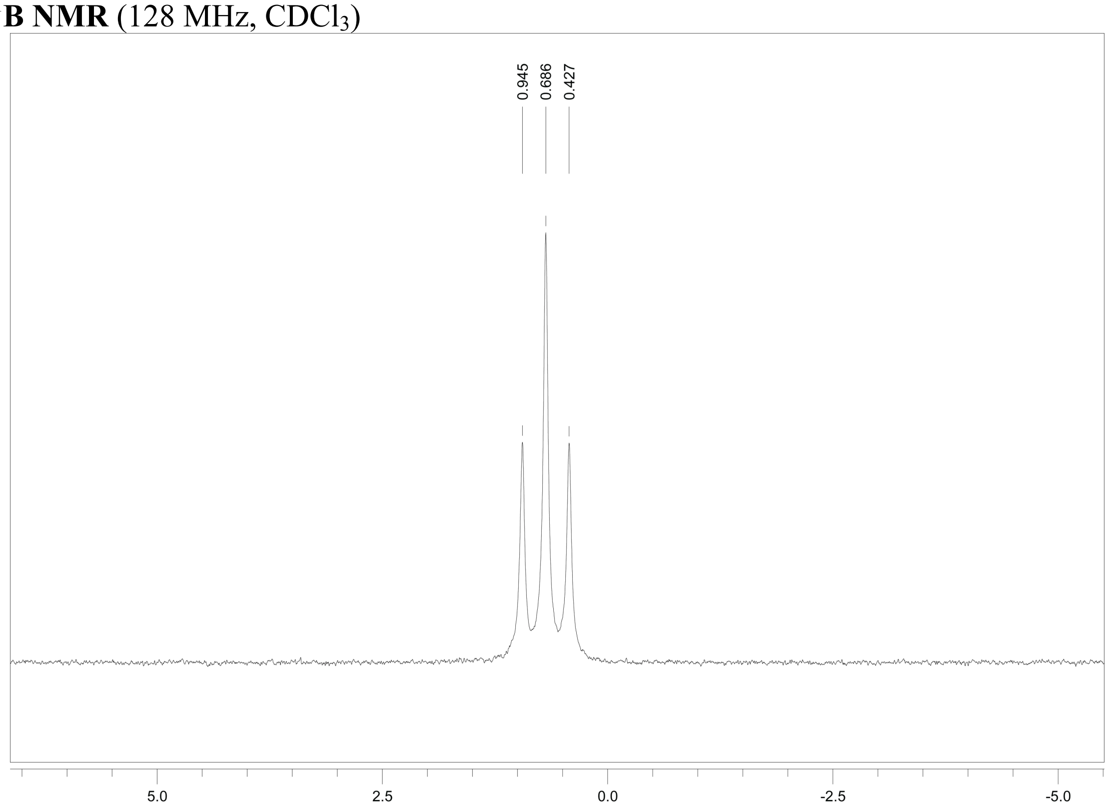
[13]C NMR (75 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

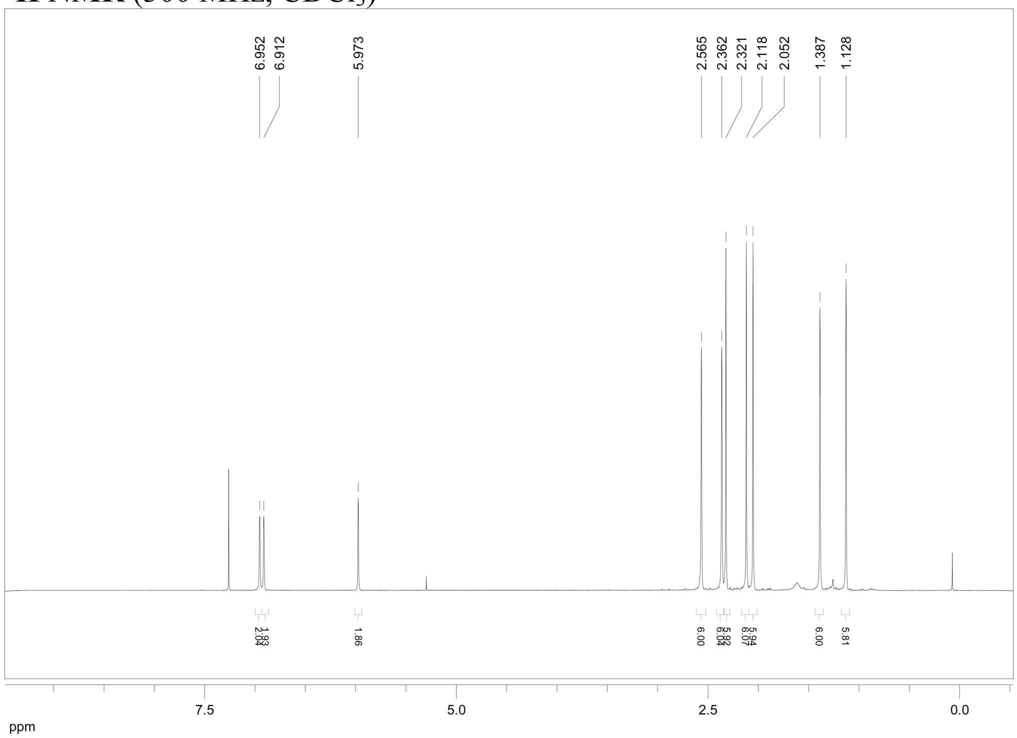


^{11}B NMR (128 MHz, $CDCl_3$)

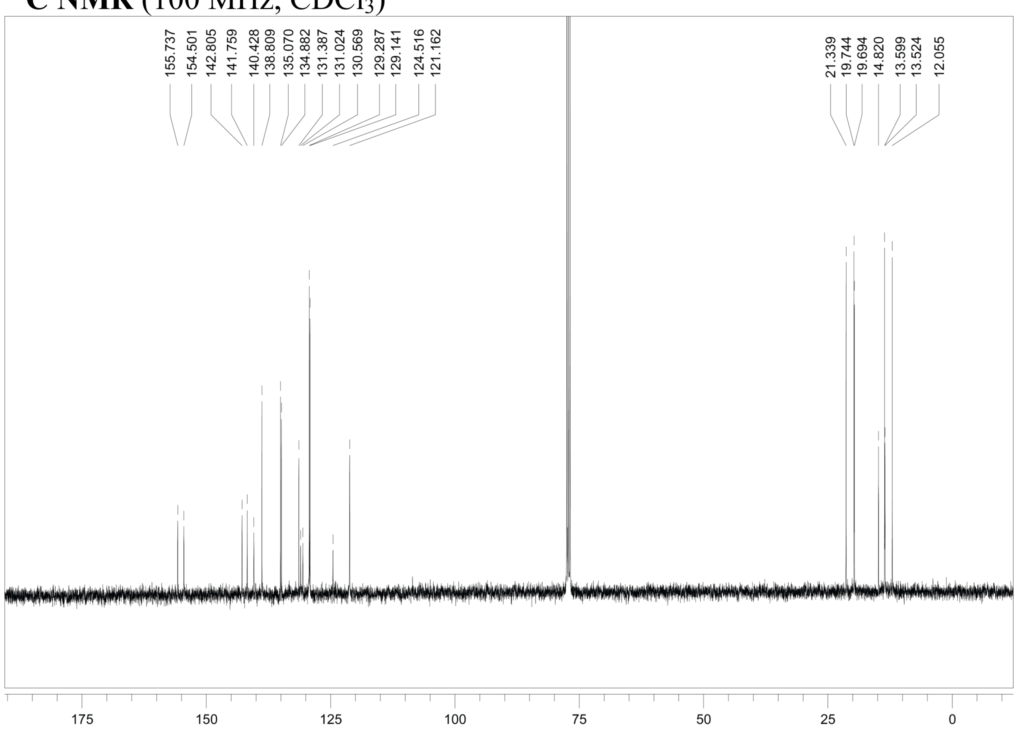


Dimer 2

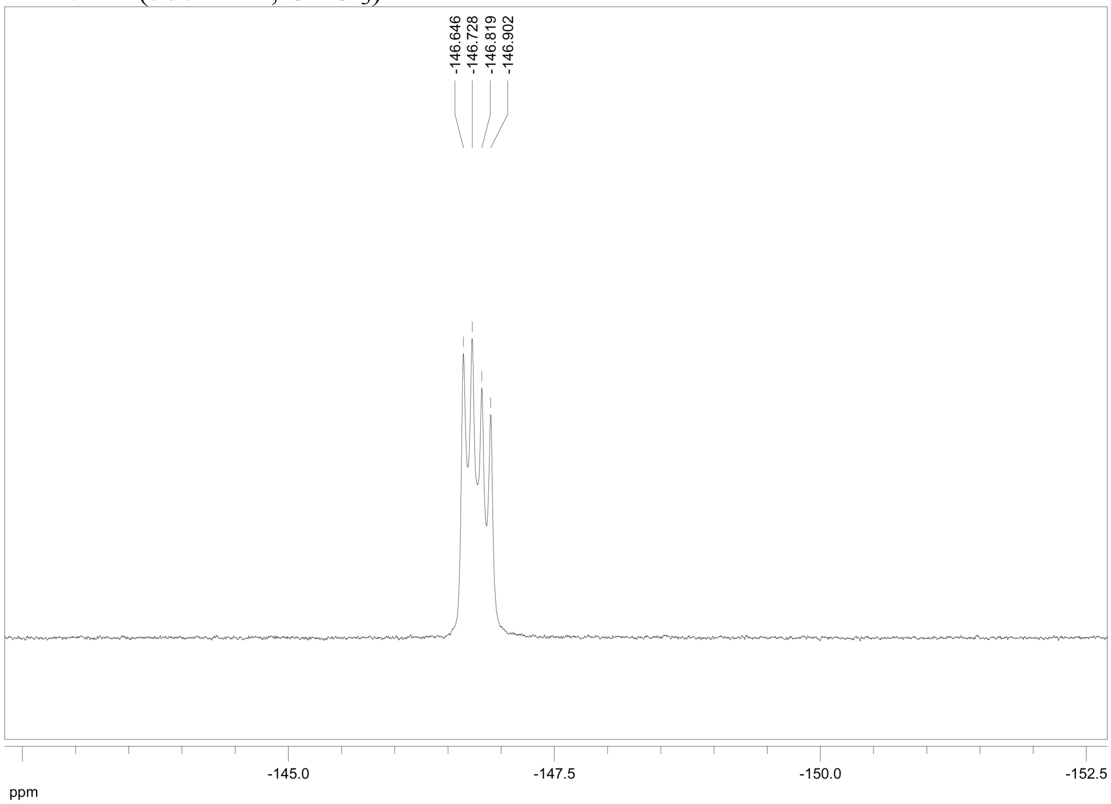
¹H NMR (300 MHz, $CDCl_3$)



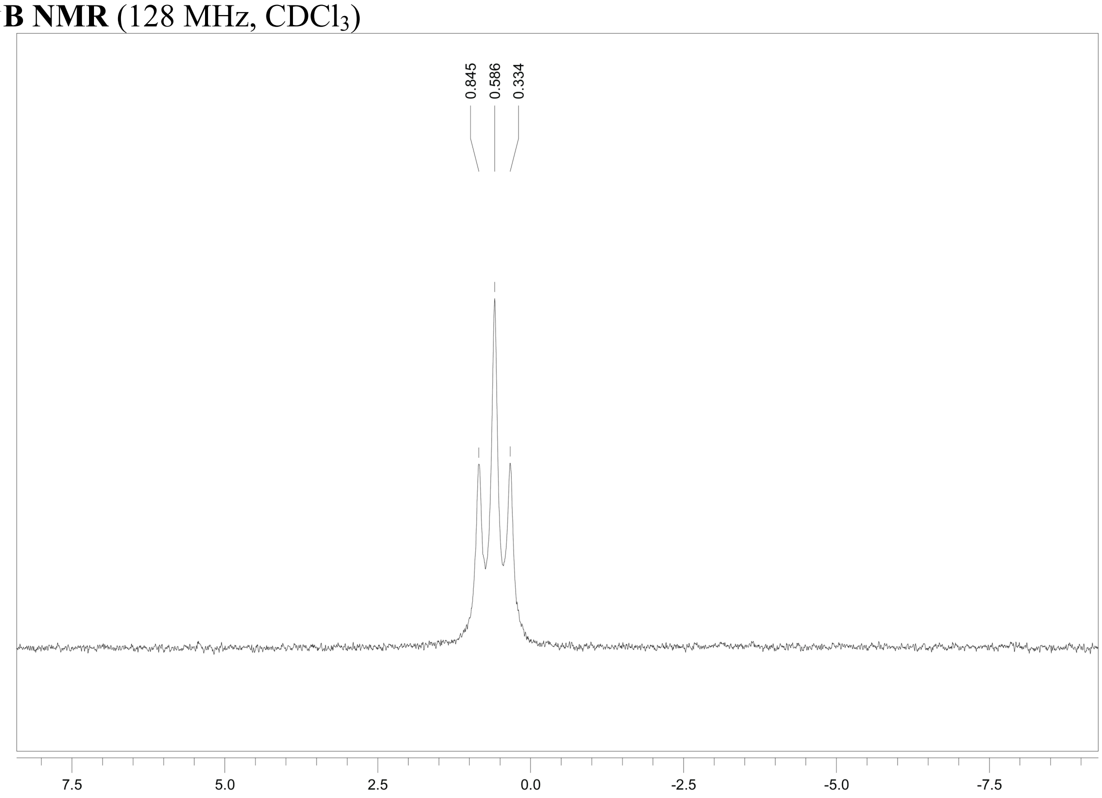
¹³C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

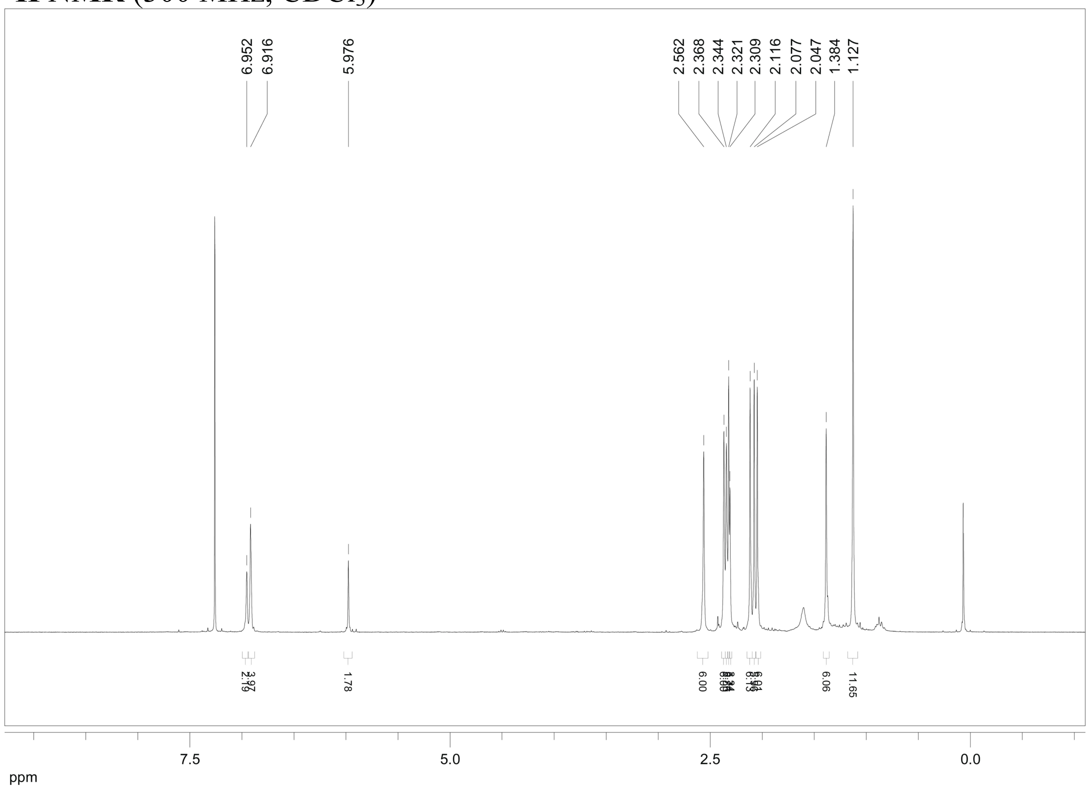


^{11}B NMR (128 MHz, $CDCl_3$)

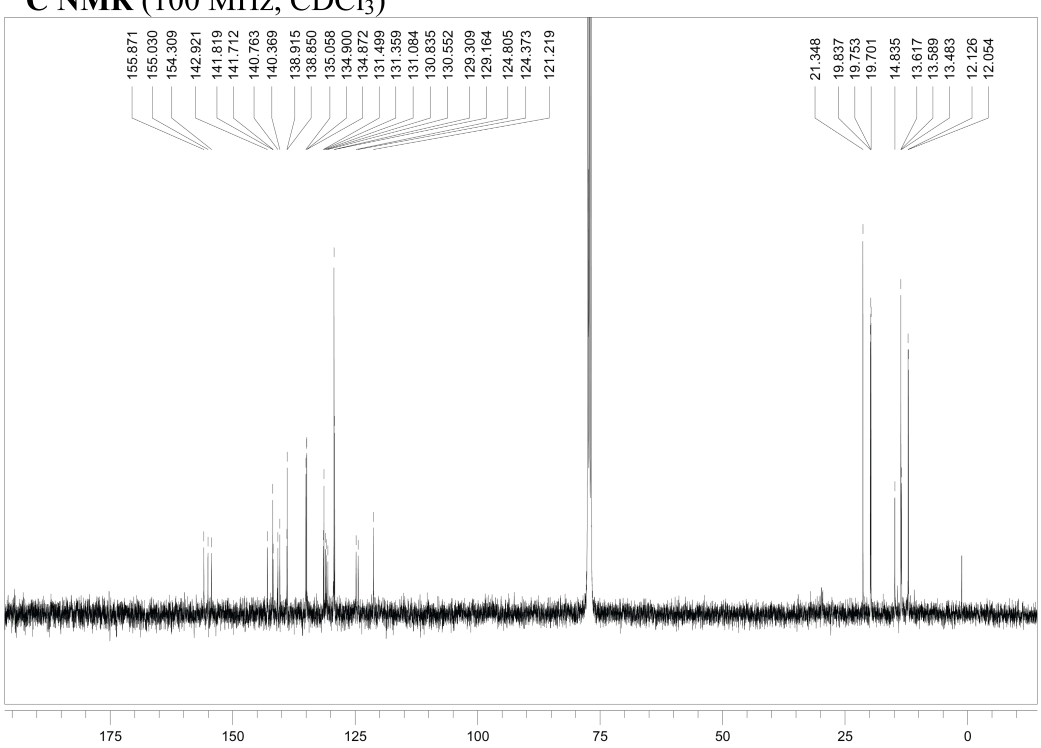


Trimer 2

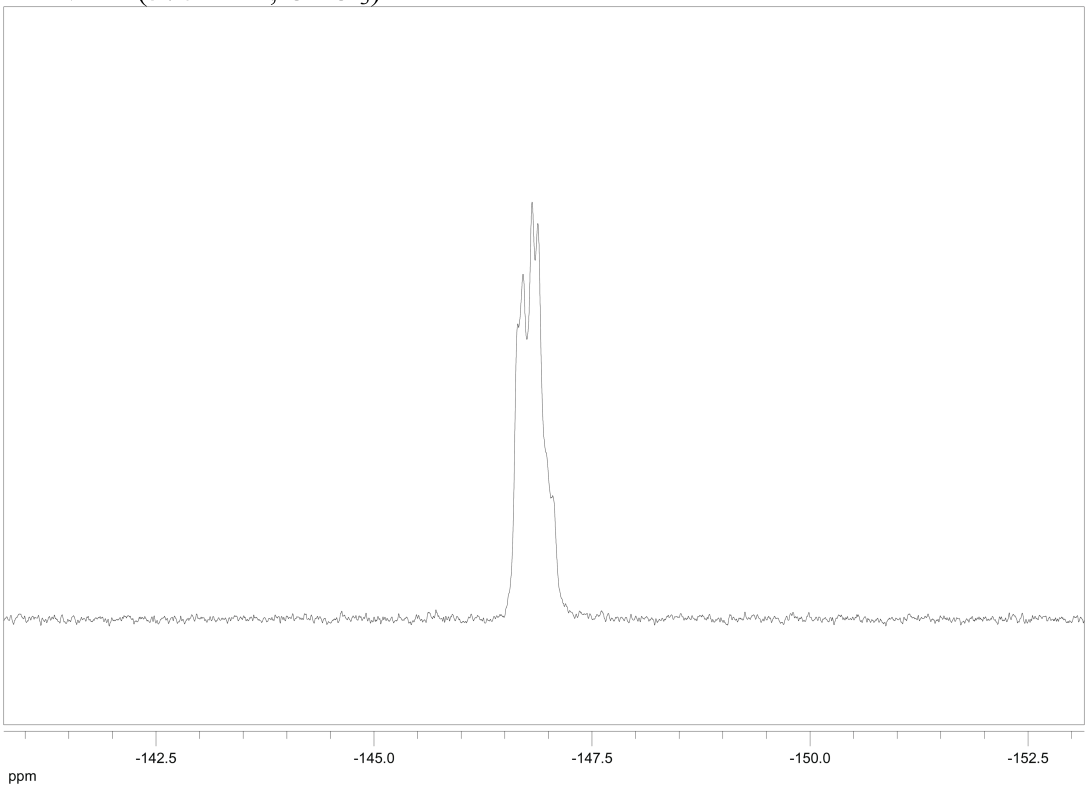
^{1}H NMR (300 MHz, $CDCl_3$)



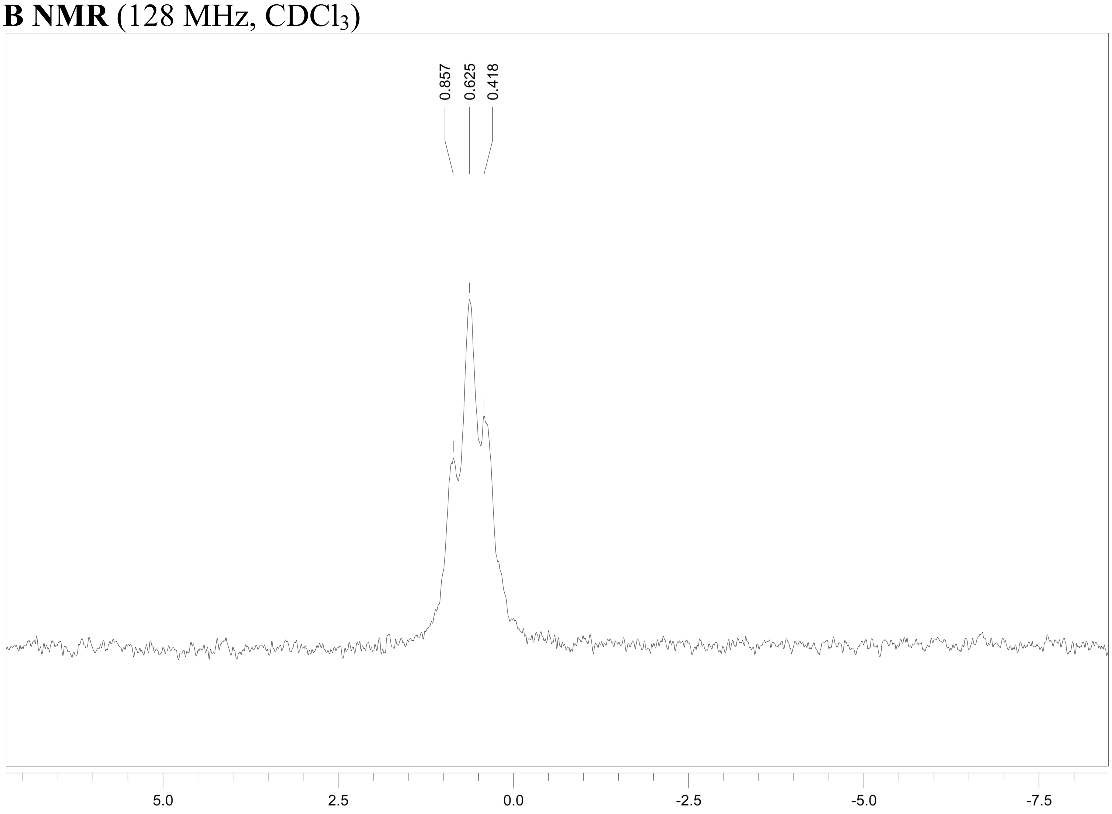
^{13}C NMR (100 MHz, $CDCl_3$)



^{19}**F NMR** (376 MHz, $CDCl_3$)

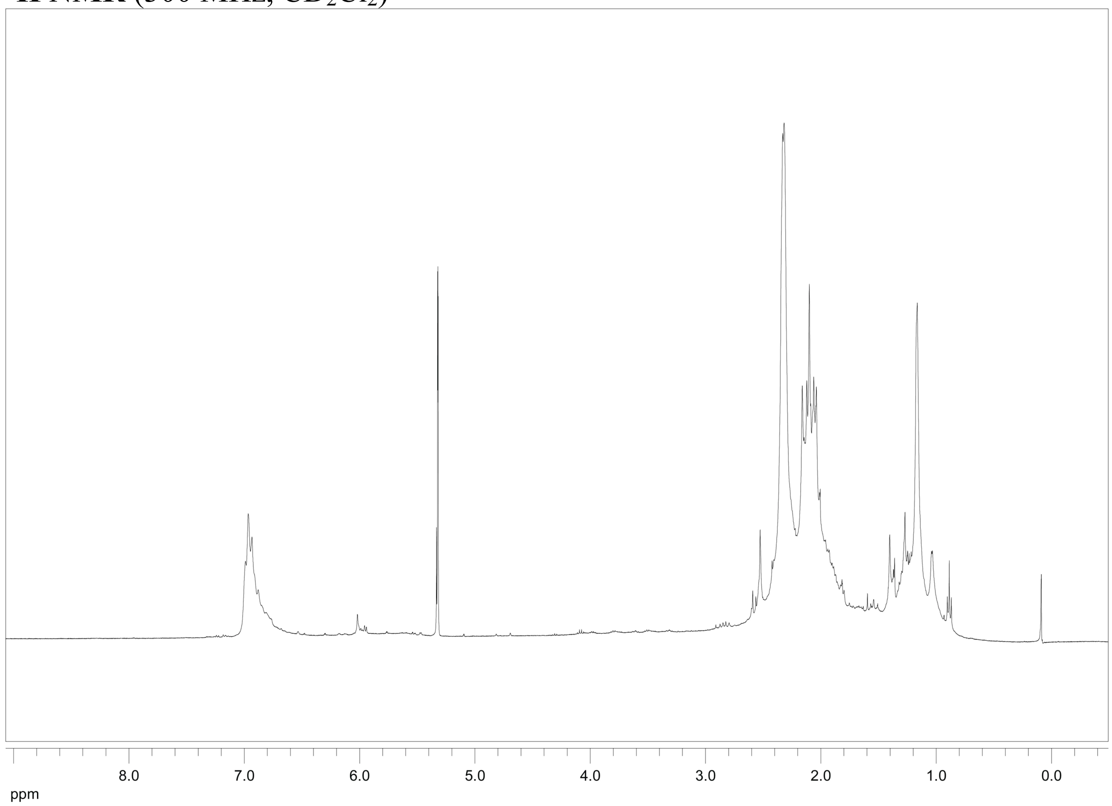


^{11}**B NMR** (128 MHz, $CDCl_3$)

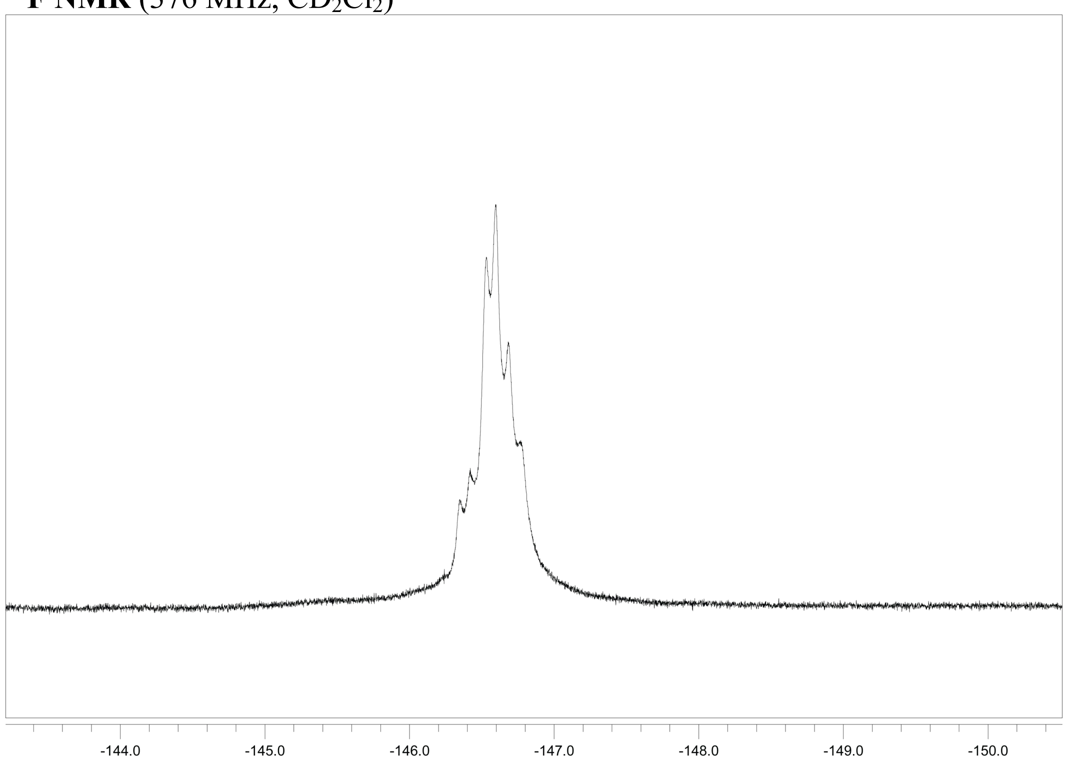


Polymer

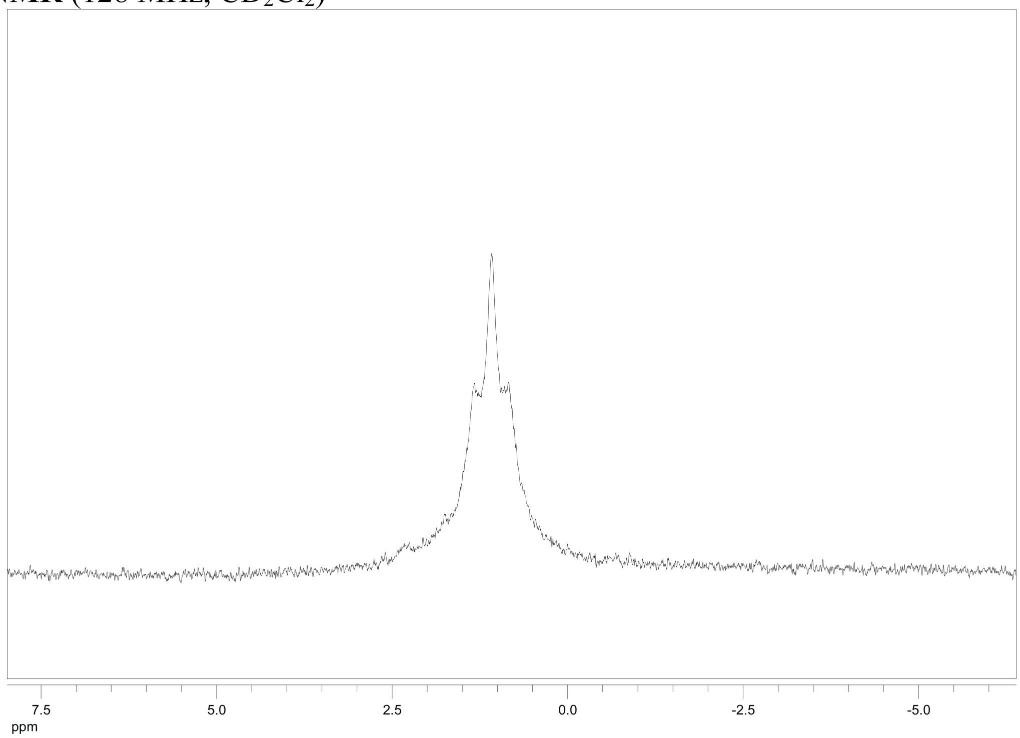
^{1}H NMR (300 MHz, CD_2Cl_2)



^{19}F NMR (376 MHz, CD_2Cl_2)

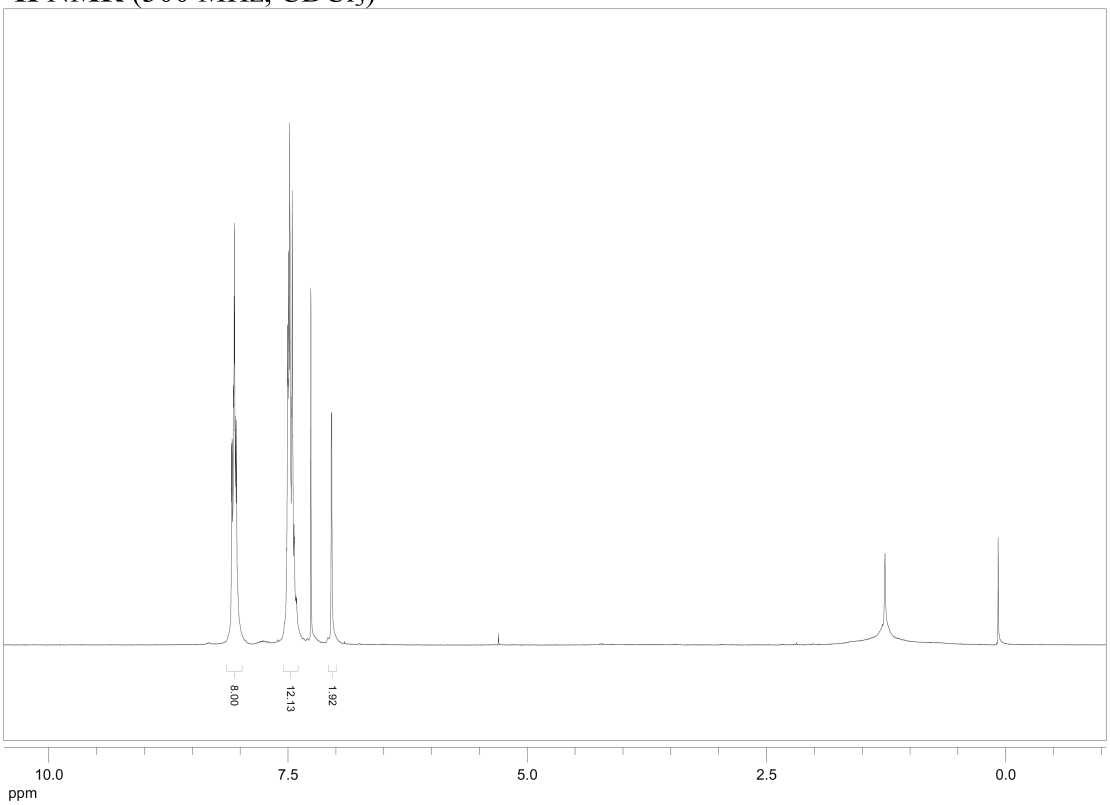


^{11}B NMR (128 MHz, CD_2Cl_2)

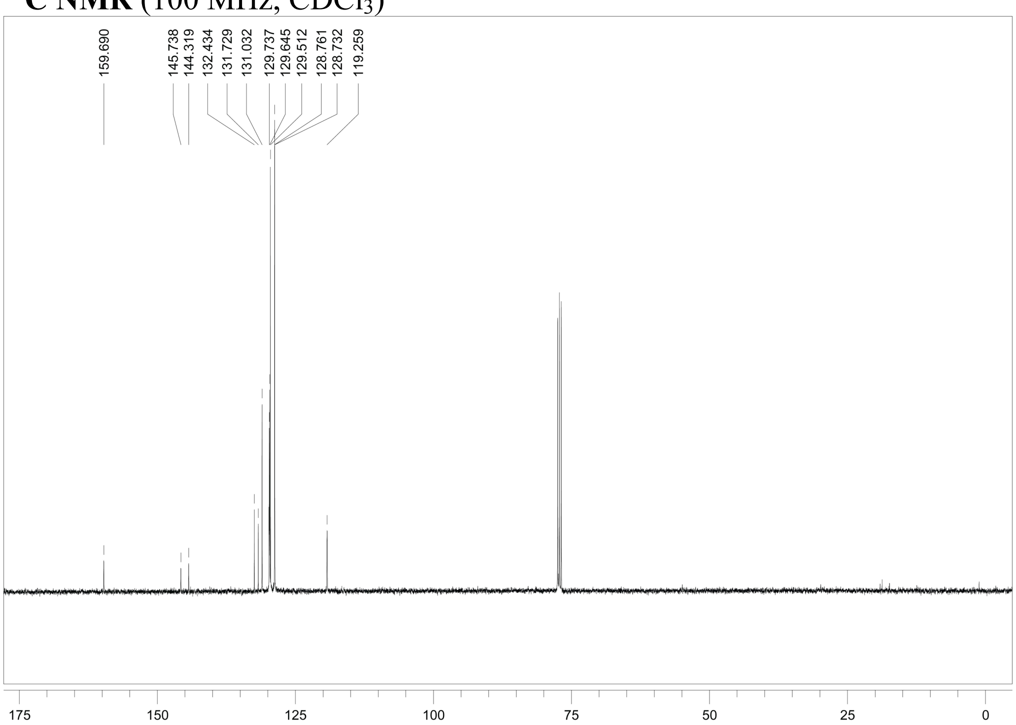


Aza-BODIPY monomer

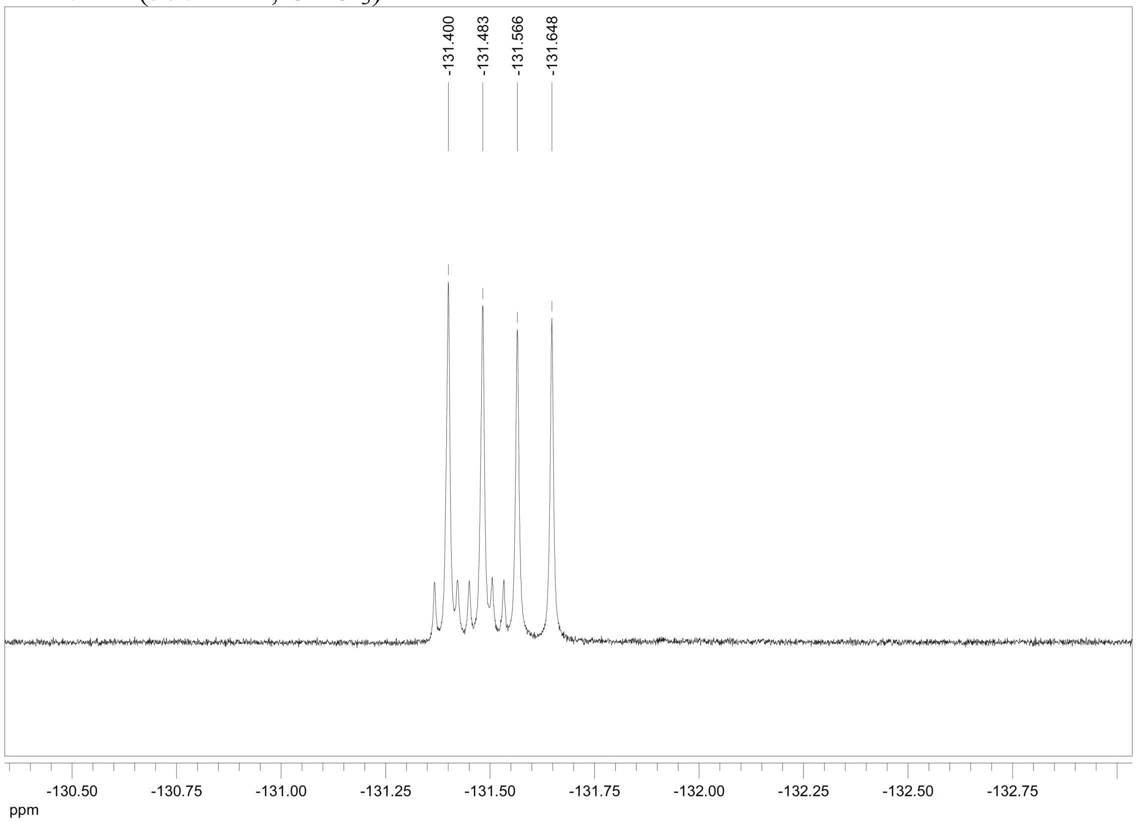
¹H NMR (300 MHz, $CDCl_3$)



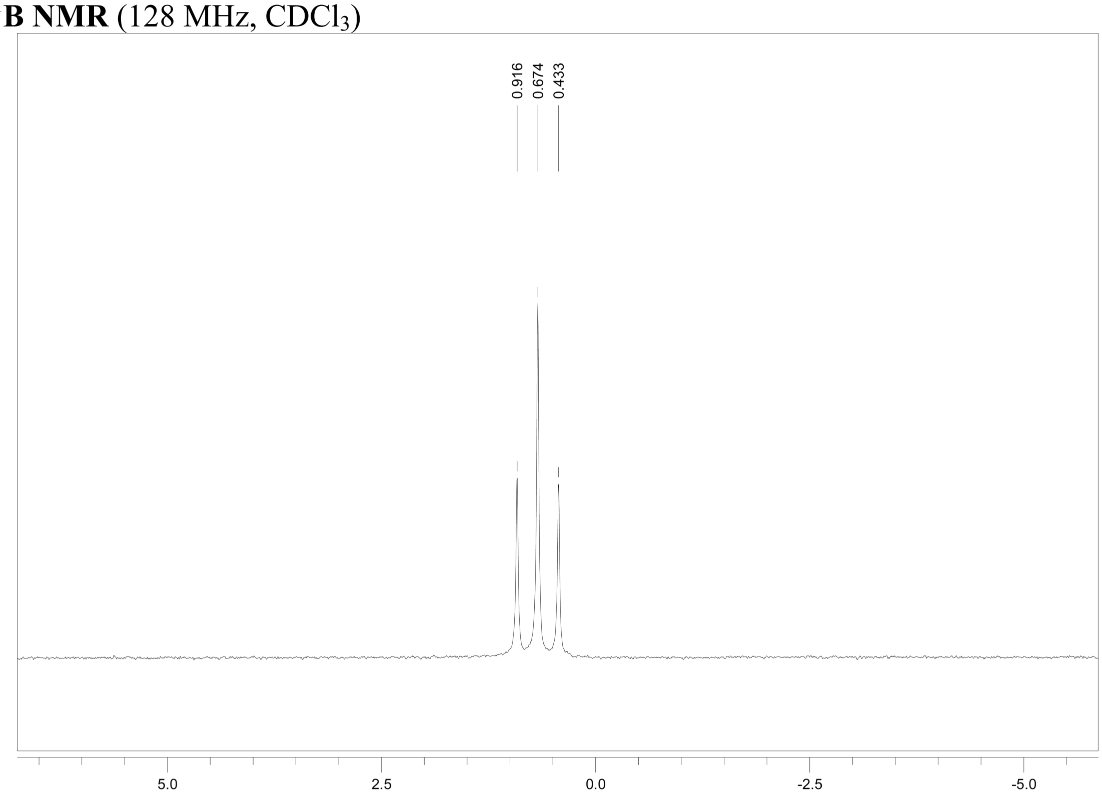
¹³C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)

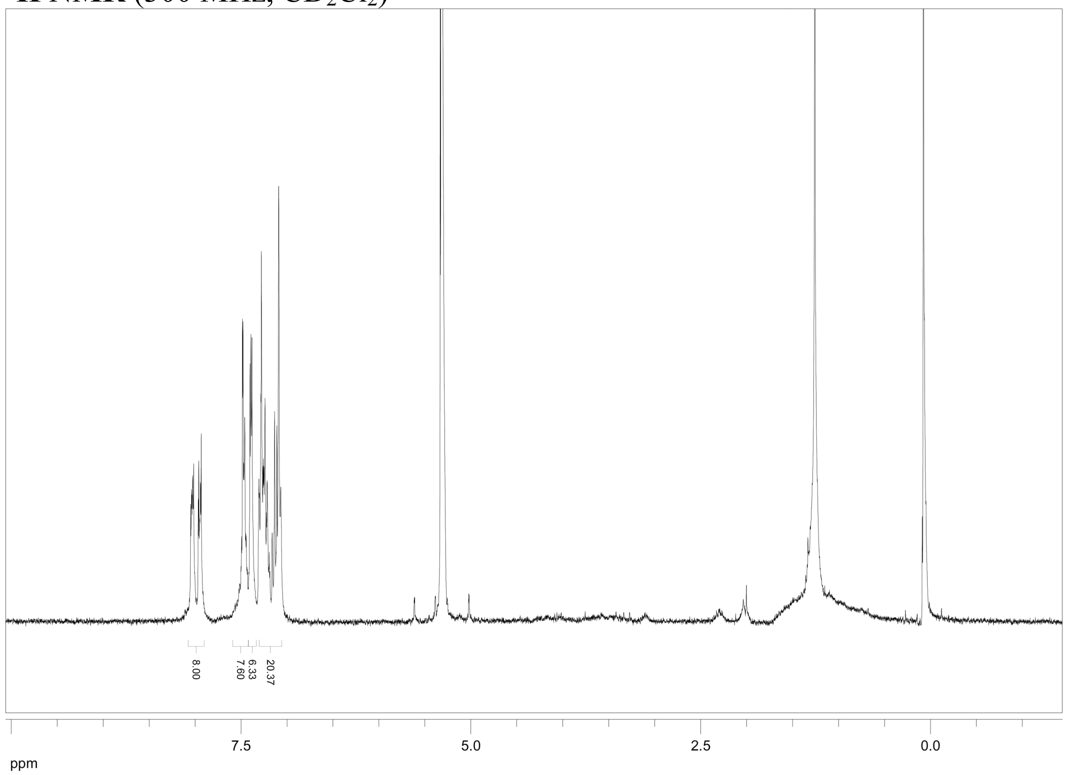


^{11}B NMR (128 MHz, $CDCl_3$)

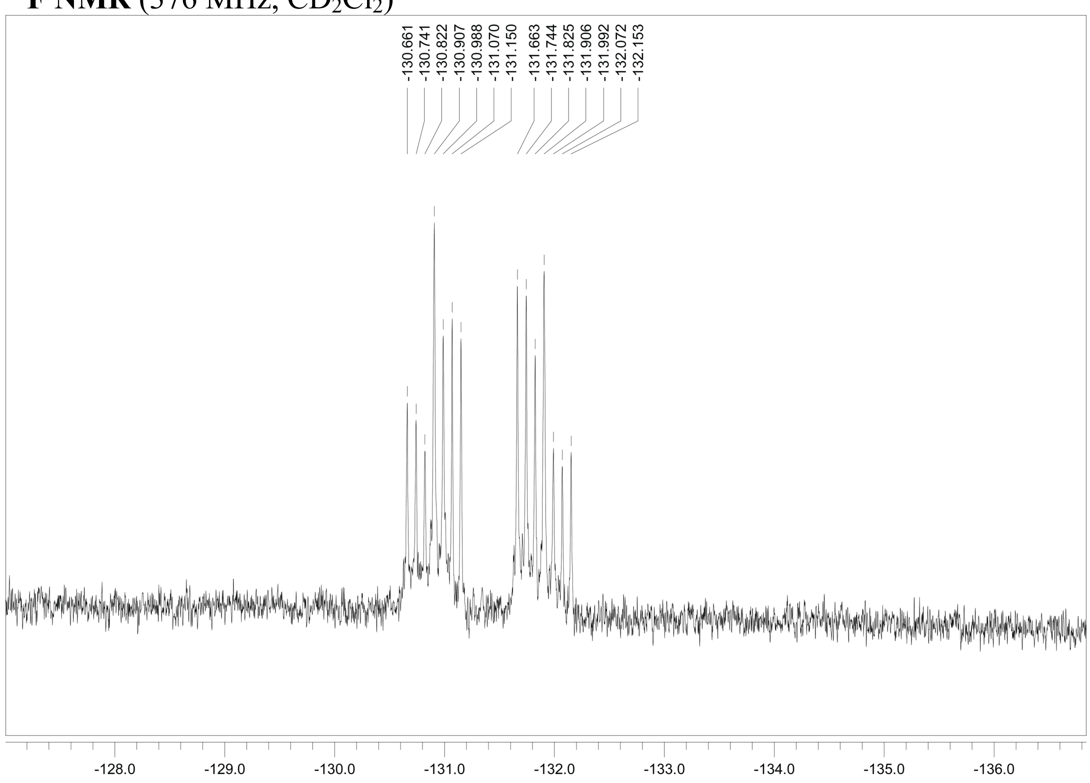


Aza-BODIPY dimer

^{1}H NMR (300 MHz, CD_2Cl_2)



^{19}F NMR (376 MHz, CD_2Cl_2)



^{11}**B NMR** (128 MHz, CD_2Cl_2)