Electronic Supplementary Material (ESI) for Chemical Science

Supporting information

Electrochemistry and Electrogenerated Chemiluminescence of Thiophene and Fluorene Oligomers. Electrochemical Formation of Oligomers on Oxidation in the Presence of Benzoyl Peroxide.

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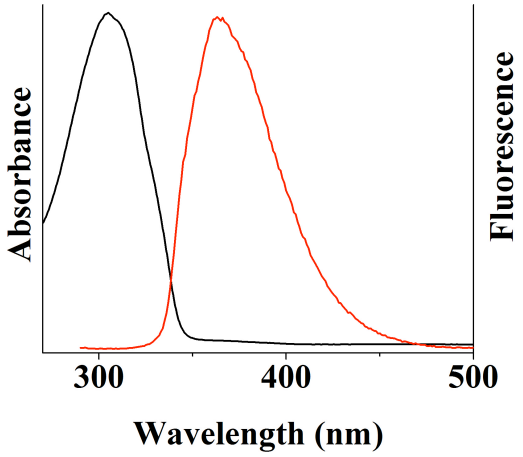
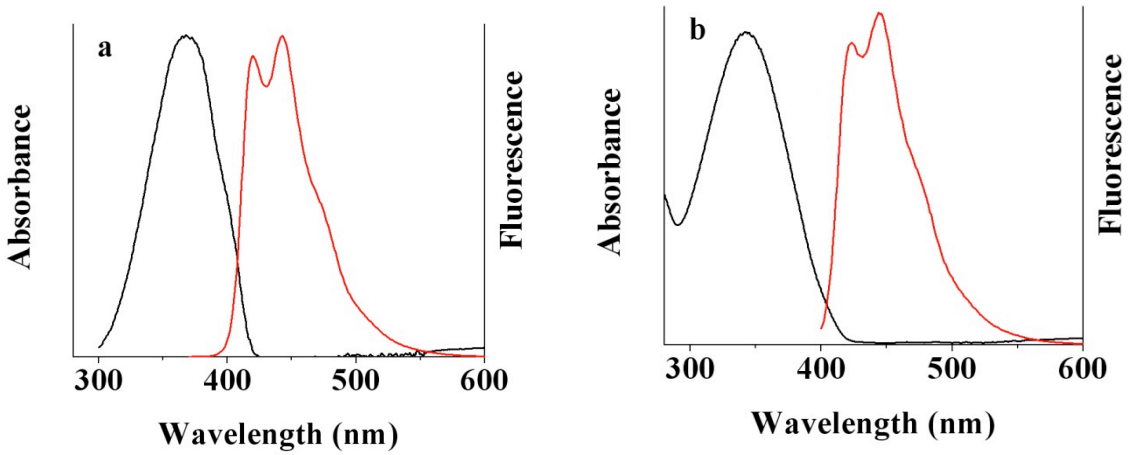


Figure S1. Absorbance and fluorescence spectra of 2 μM **t-dimer-1**.



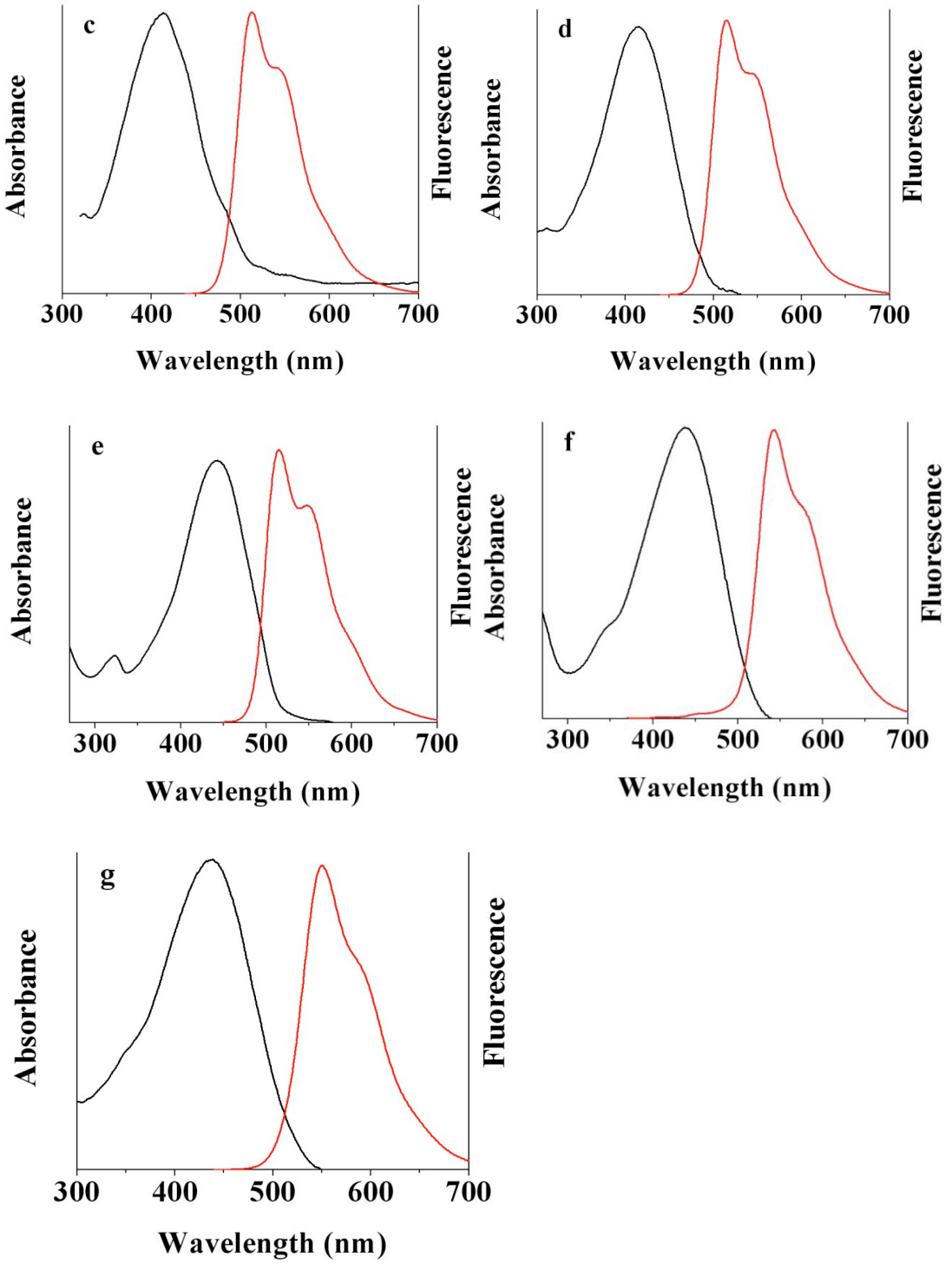
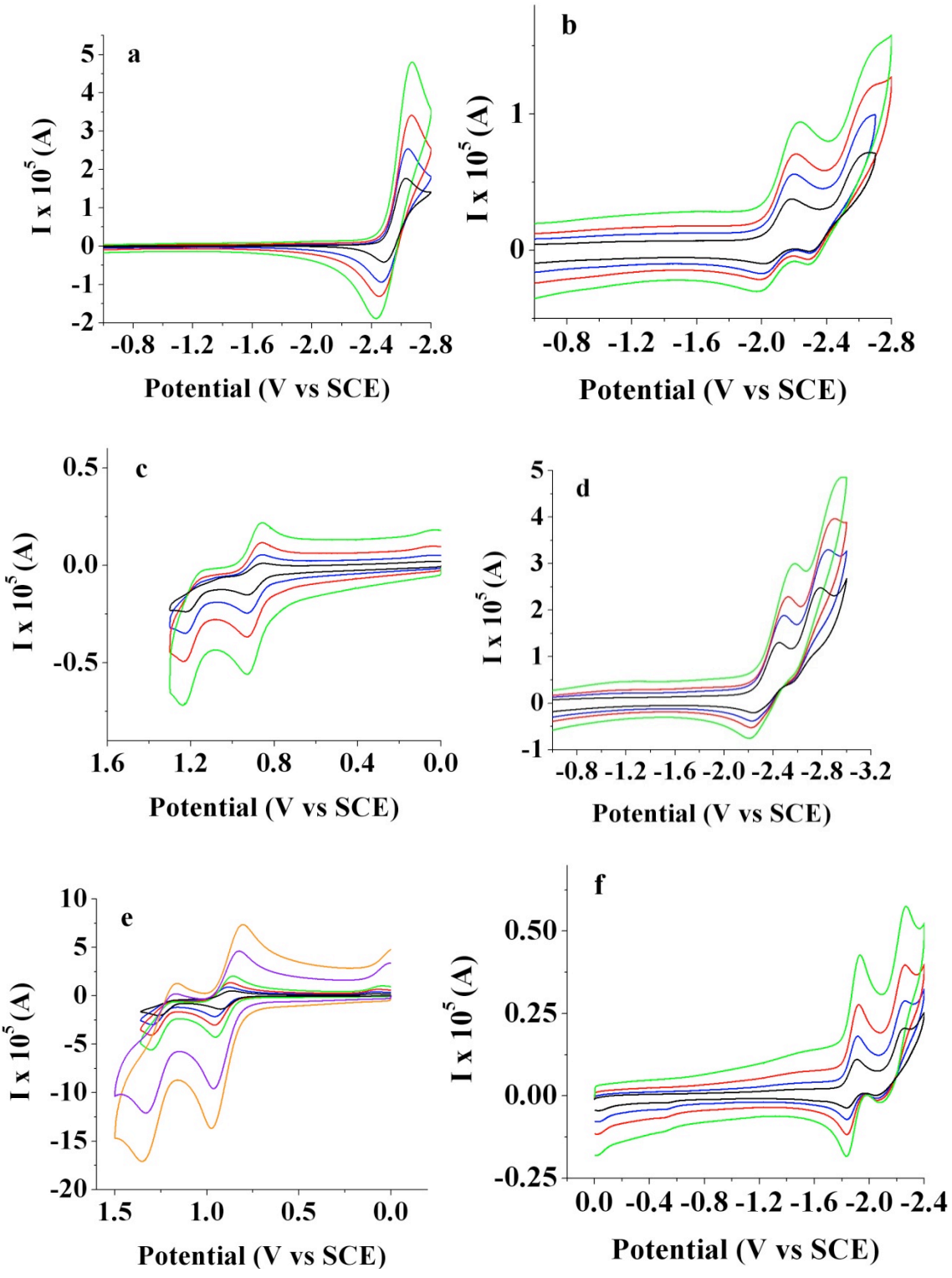
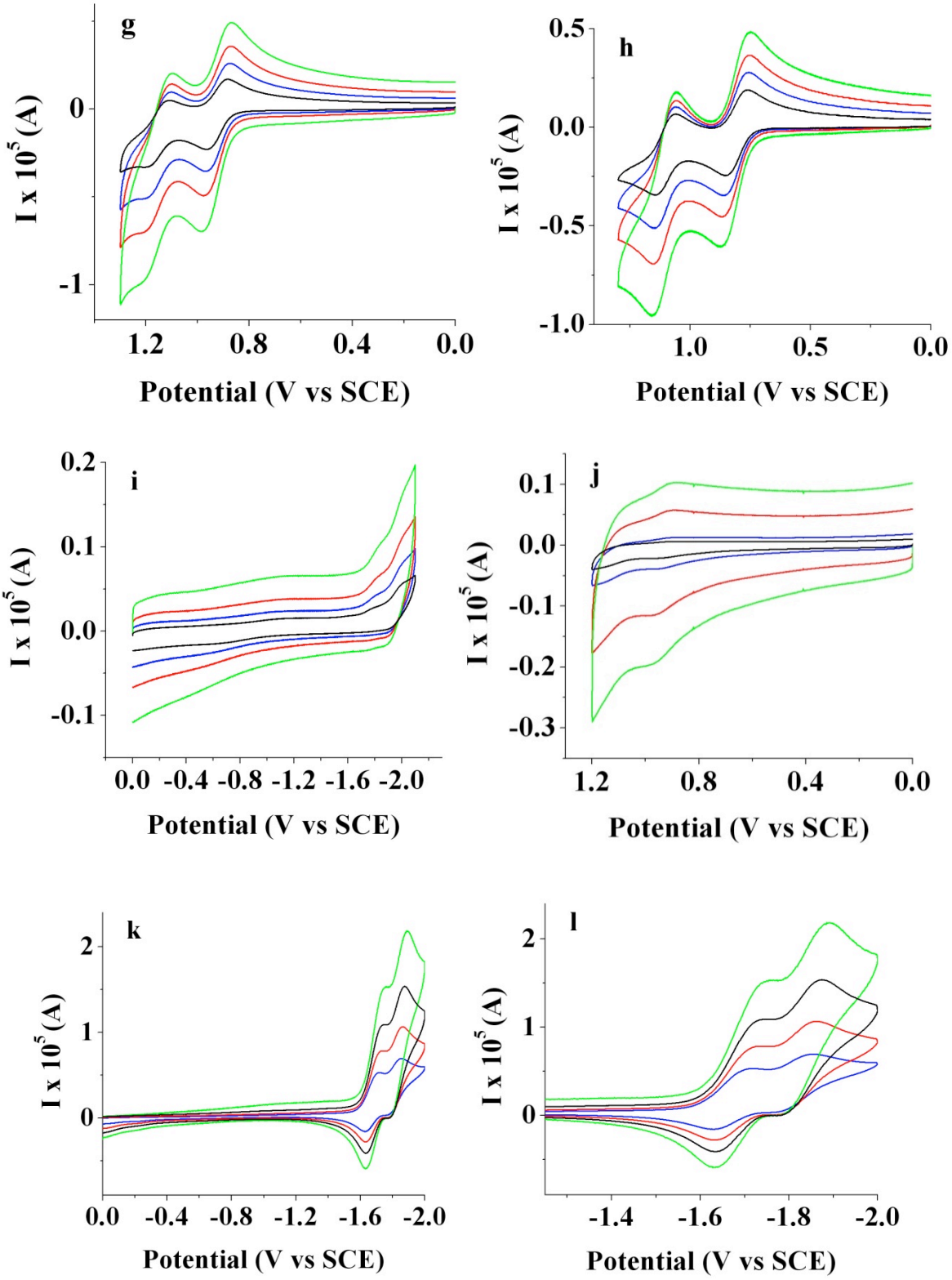
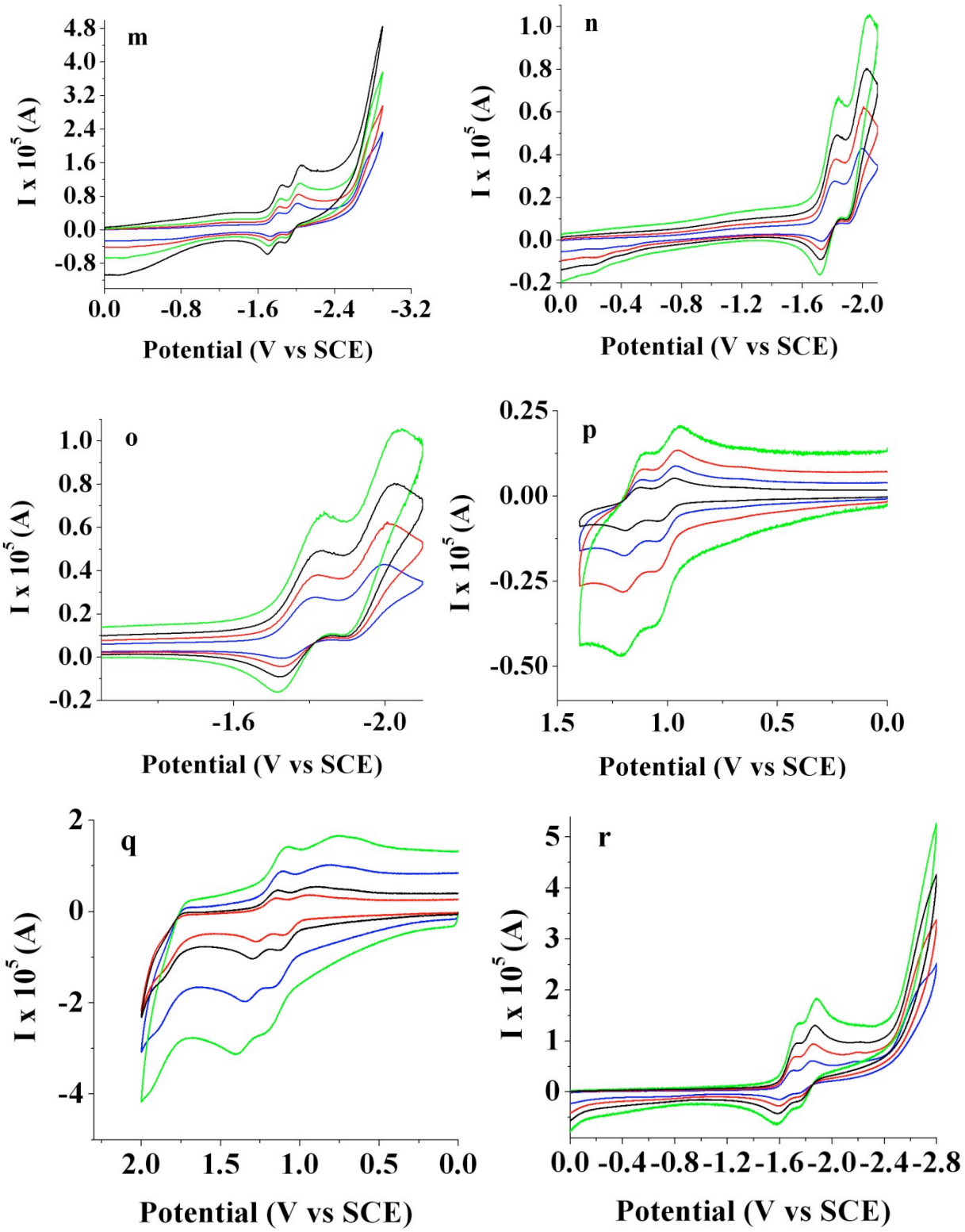


Figure S2. Absorption (black) and fluorescence (red) spectra of 2 μM thiophene dyes in DCM: (a) **t-trimer-1**; (b) **t-trimer-2** (c) **t-hexamer-1**; (d) **t-hexamer-2:** (e) **t-hexamer-3**; (f) **t-octamer**; (g) **t-nonamer.**







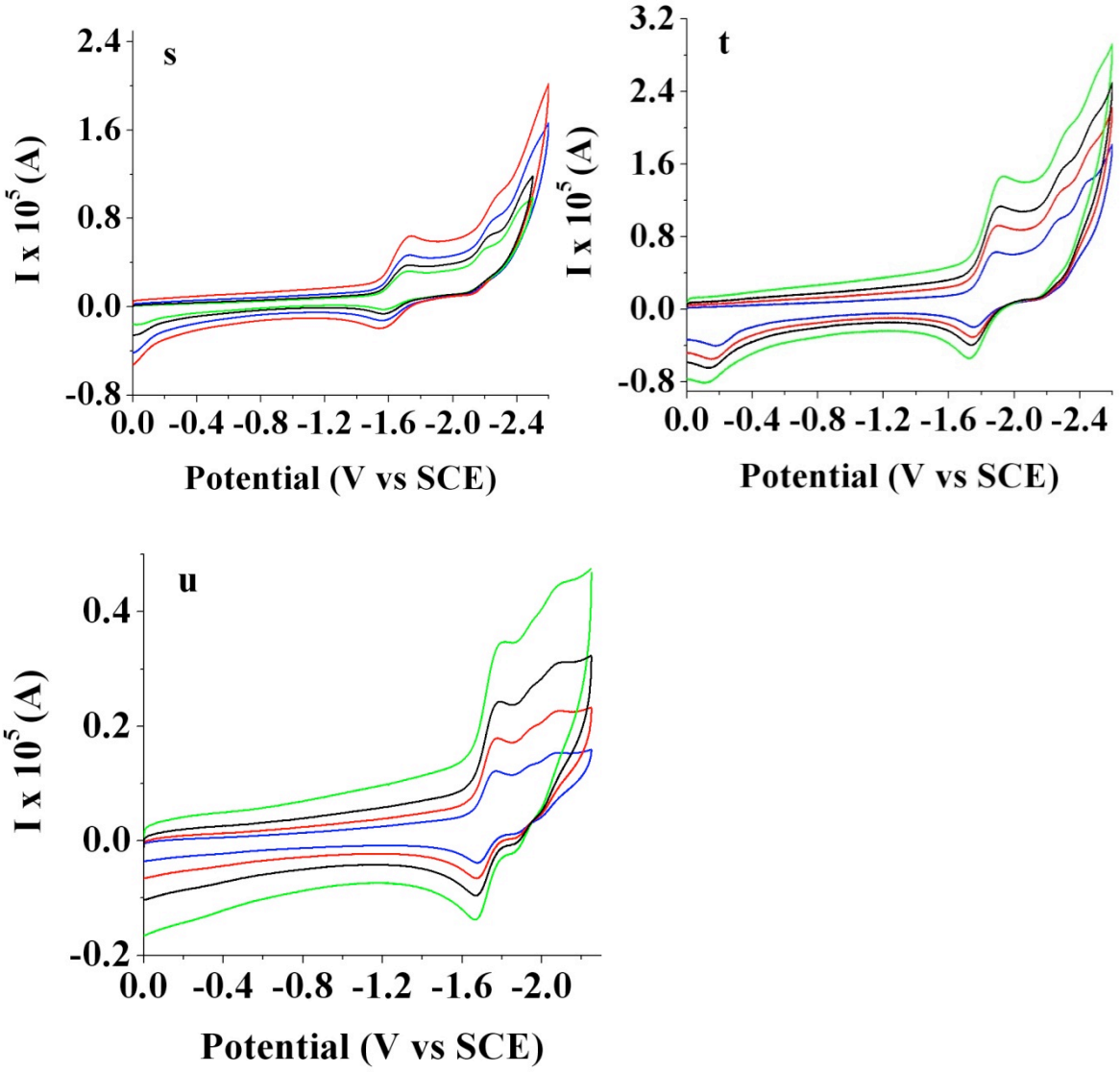


Figure S3. Scan rate dependence for the corresponding dyes: (a) 2.5 mM **t-dimer**; (b) 0.15 mM and (c) 0.22 mM **t-trimer-1**; (d) 0.6 mM and (e) 1.9 mM **t-trimer-2**; (f) 0.15 mM, (g) 0.28 mM and (h) 0.34 mM **t-tetramer**; (i) and (j) 0.05 mM **t-hexamer-1**; (k), (l) 0.7 mM **t-hexamer-2** and (m) 0.5 mM **t-hexamer-2**; (n), (o) 0.3 mM **t-hexamer-3**, (p) 0.15 mM **t-hexamer-3**, (q) 0.5 mM **t-hexamer-3** and (r) 0.8 mM **t-hexamer-3**; (s) 0.18 mM **t-octamer**; (t) 0.4 mM **t-nonamer**; (u) 0.15 mM **t-dodecamer**. Scan rates are shown in simulations except m, (q) and (r) where scan rates 0.1 V/s, 0.25 V/s; 0.5 V/s and 1 V/s were used. Solvent: (m), (r) THF, (q) 1:1 benzene: acetonitrile. All other parameters are also shown in simulations.

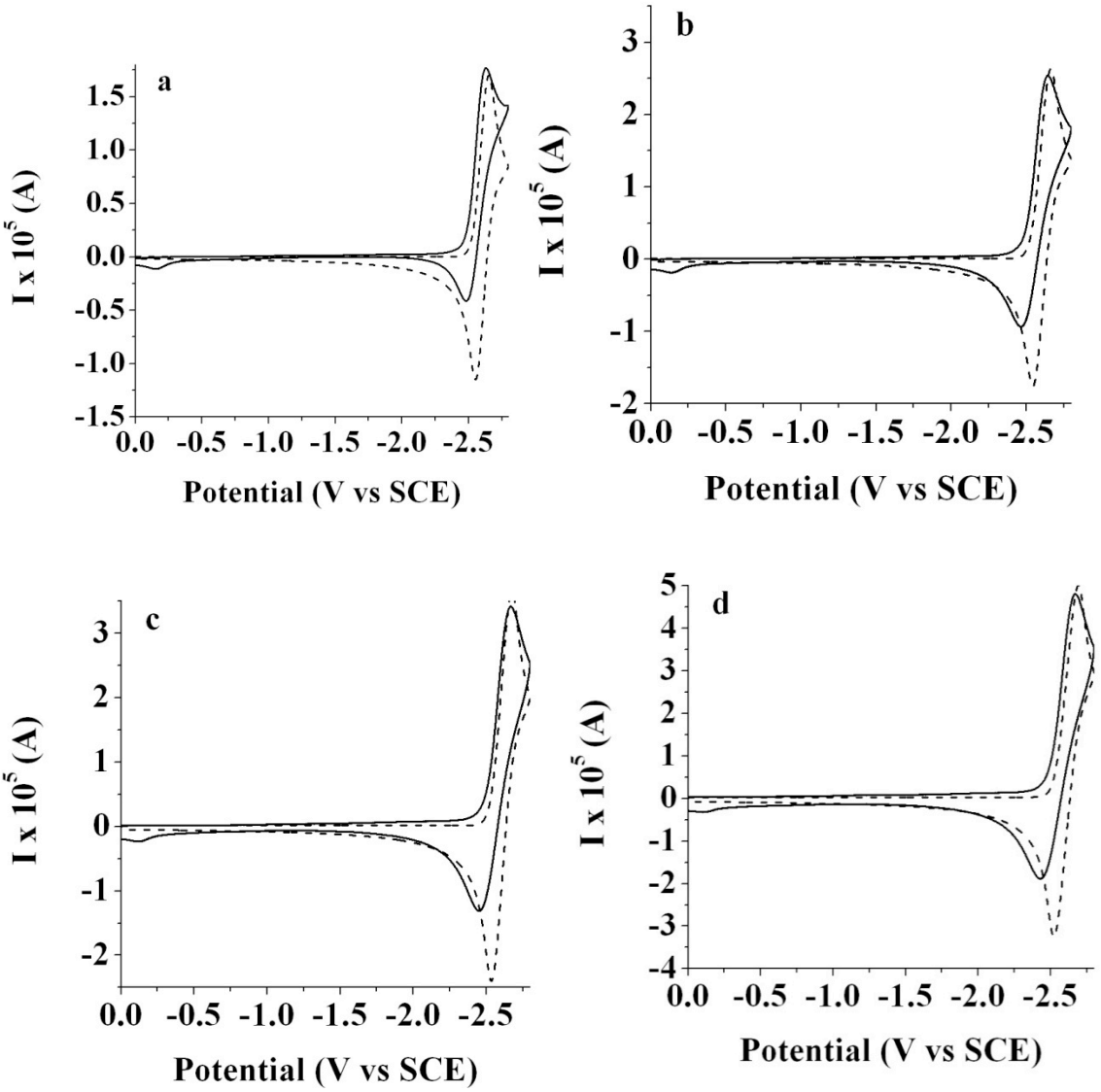
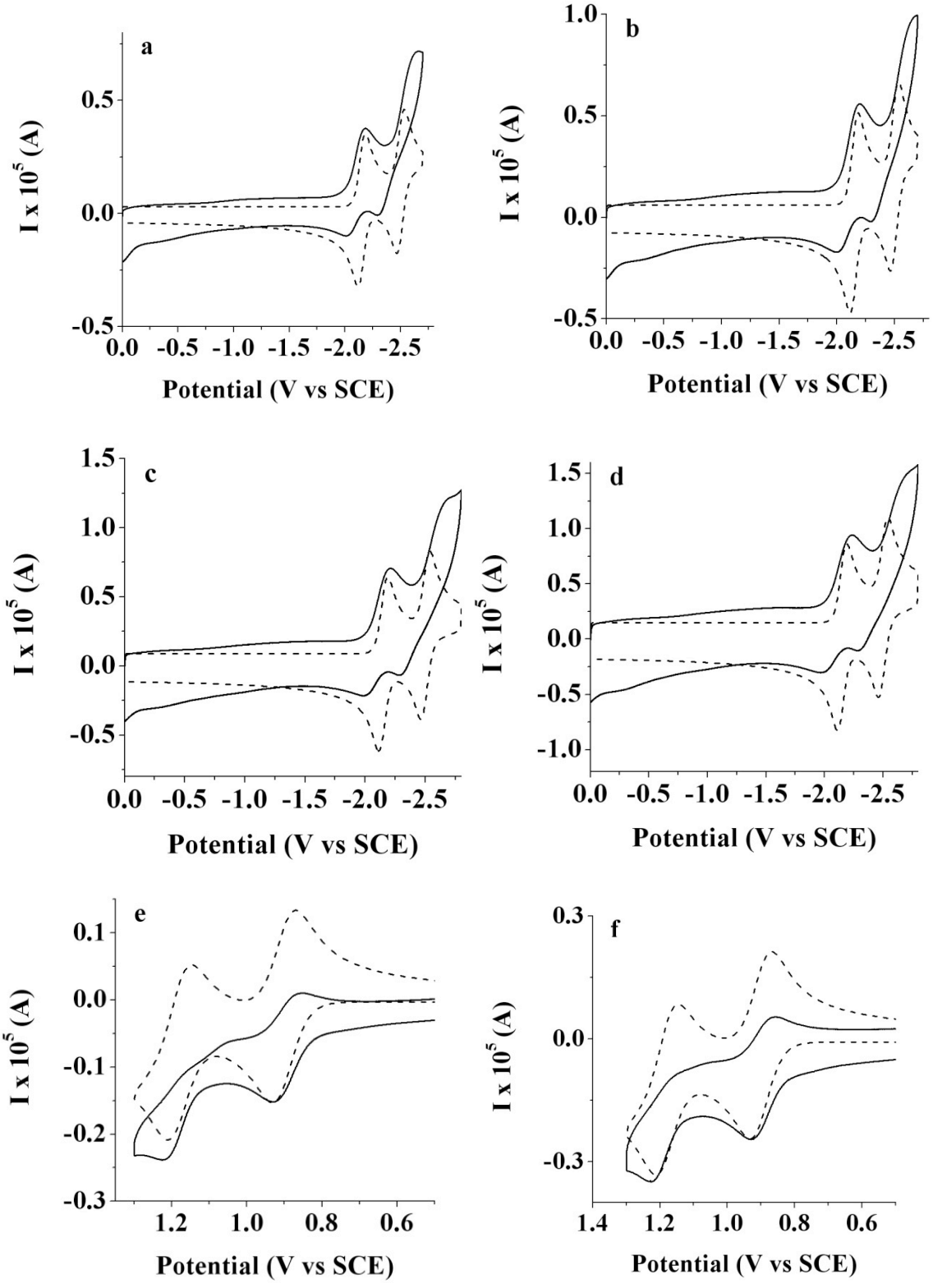


Figure S4. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 2.5 mM **t-dimer** during the scan in the negative direction (a)-(d). Scan rates for reduction (a) 0.1 V/s; (b) 0.25 V/s; (c) 0.5 V/s; (d) 1 V/s. Experimental data: solvent: THF; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 7 x 10^{-6} cm^2/s; uncompensated resistance: 1000 Ω; capacitance: 3 x 10^{-7} F.



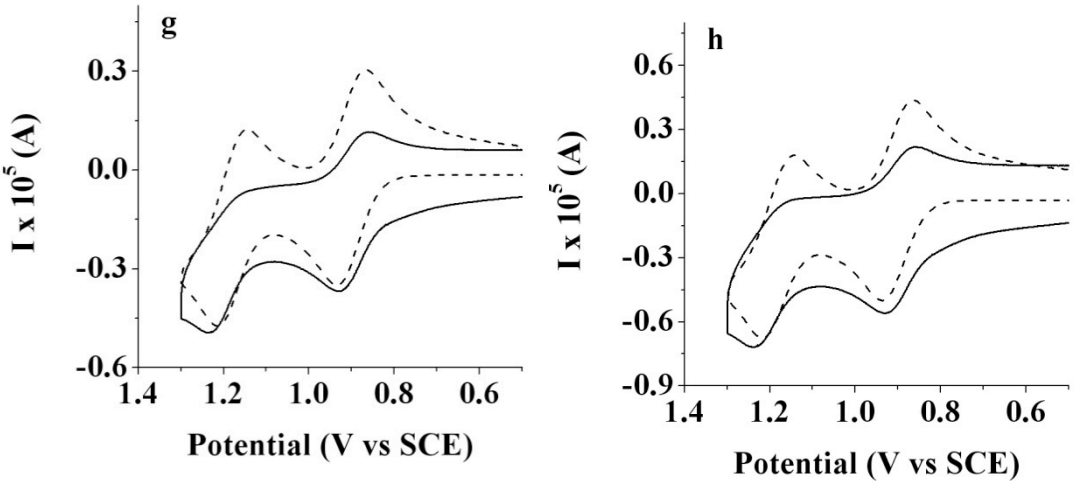
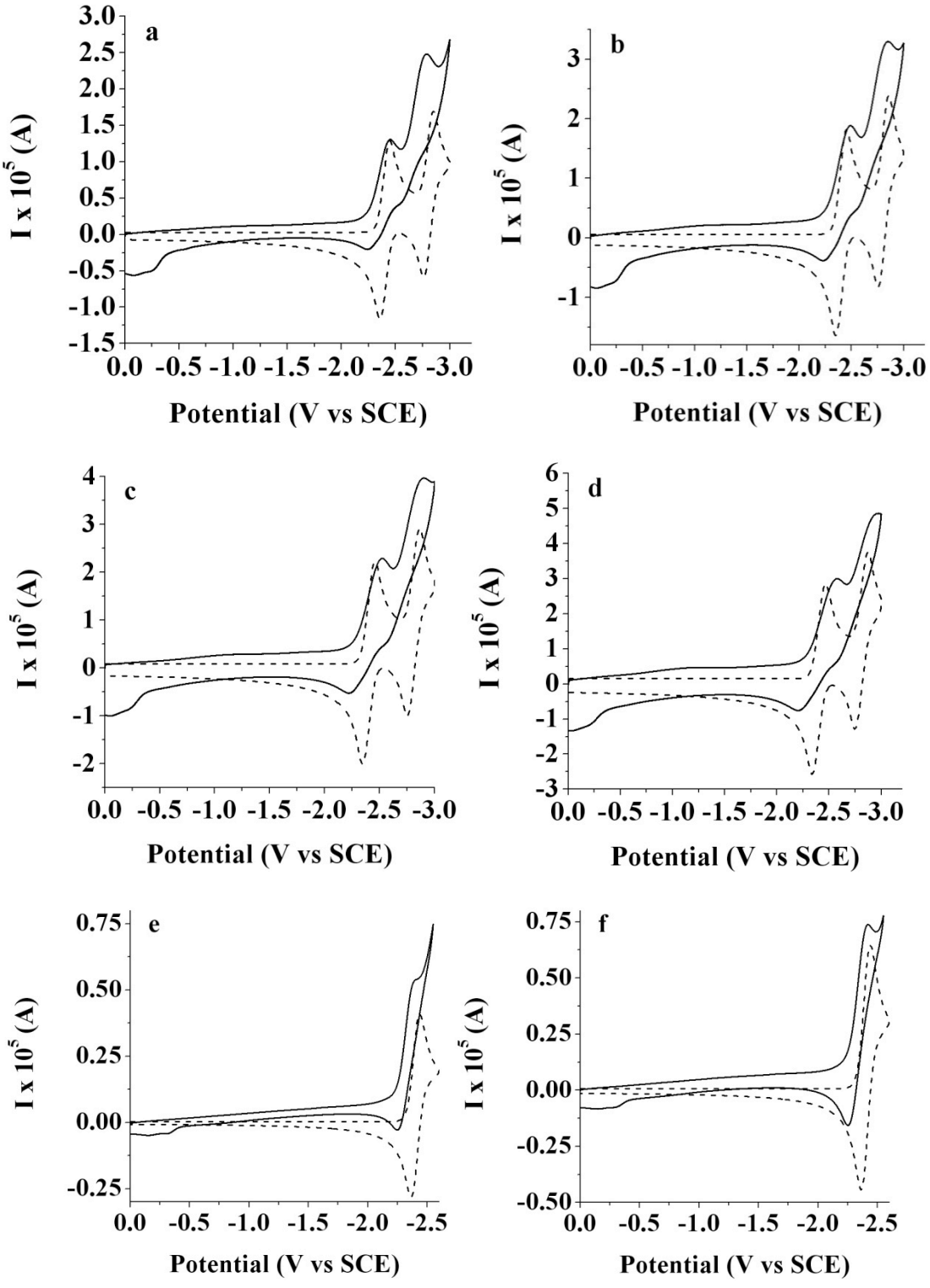
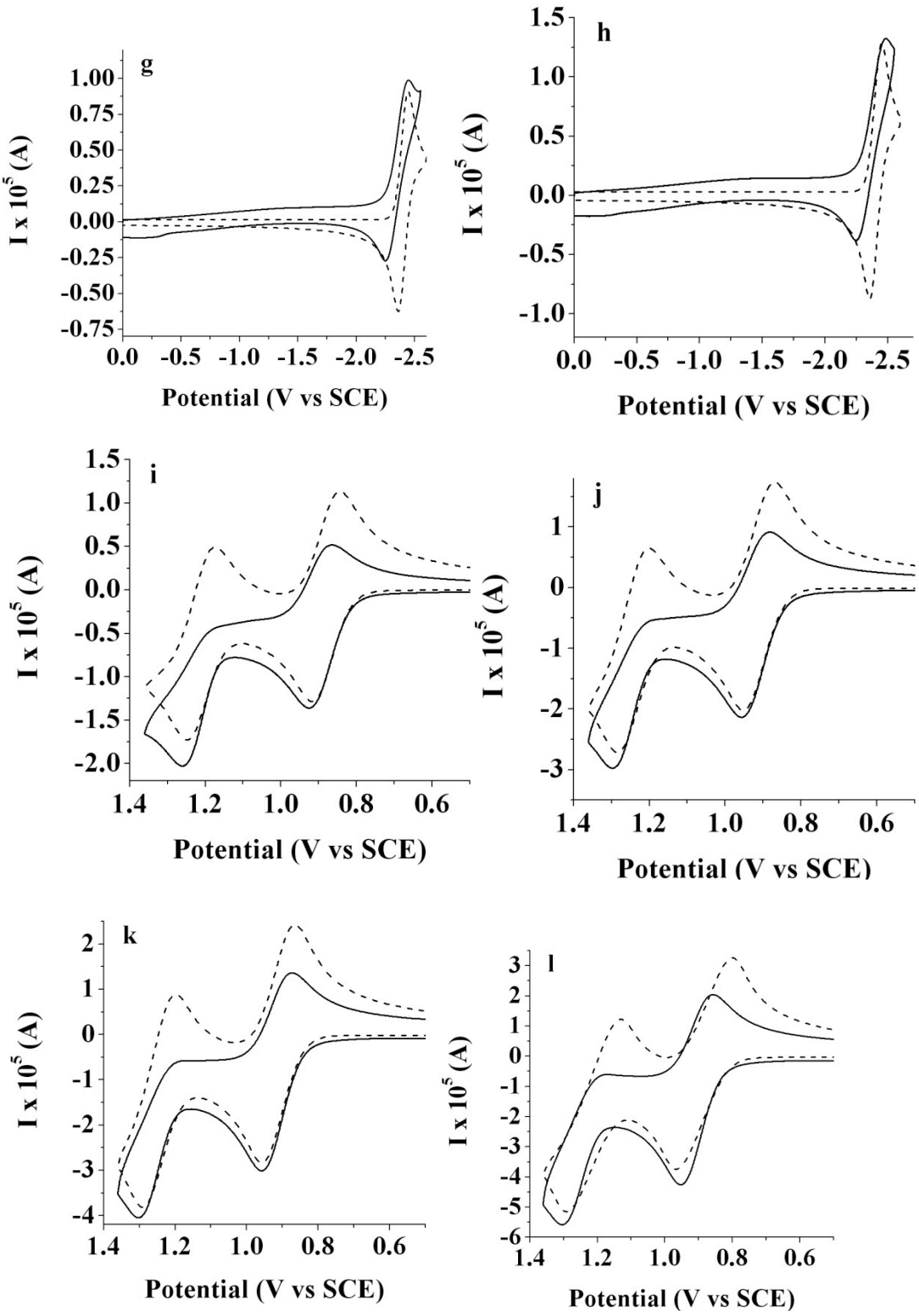


Figure S5. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.15 mM **t-trimer-1** during the scan in the negative direction (a)-(d) and 0.22 mM **t-trimer-1** during scan in the positive direction (e)-(h). Scan rates for reduction (a) 1 V/s; (b) 2 V/s; (c) 3 V/s; (d) 5 V/s; Scan rates for oxidation (e) 0.1 V/s; (f) 0.25 V/s; (g) 0.5 V/s; (h) 1 V/s. Experimental data: solvent: (a)-(d) THF, (e)-(h) 1:1 benzene: acetonitrile; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 6.6 x 10^{-6} cm^2/s; uncompensated resistance: 1000 Ω; capacitance: 3 x 10^{-7} F.





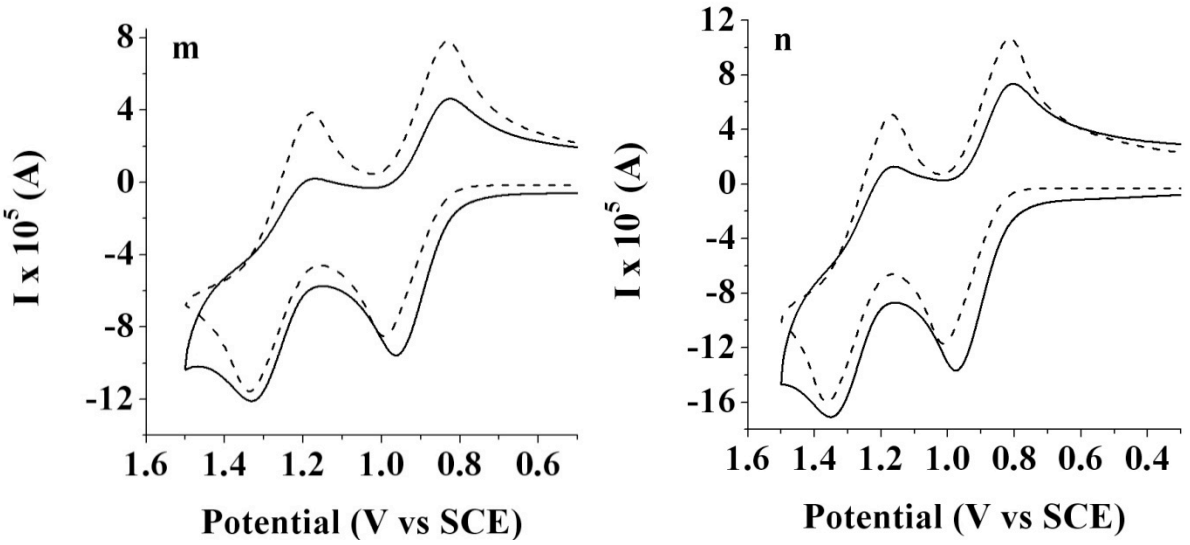
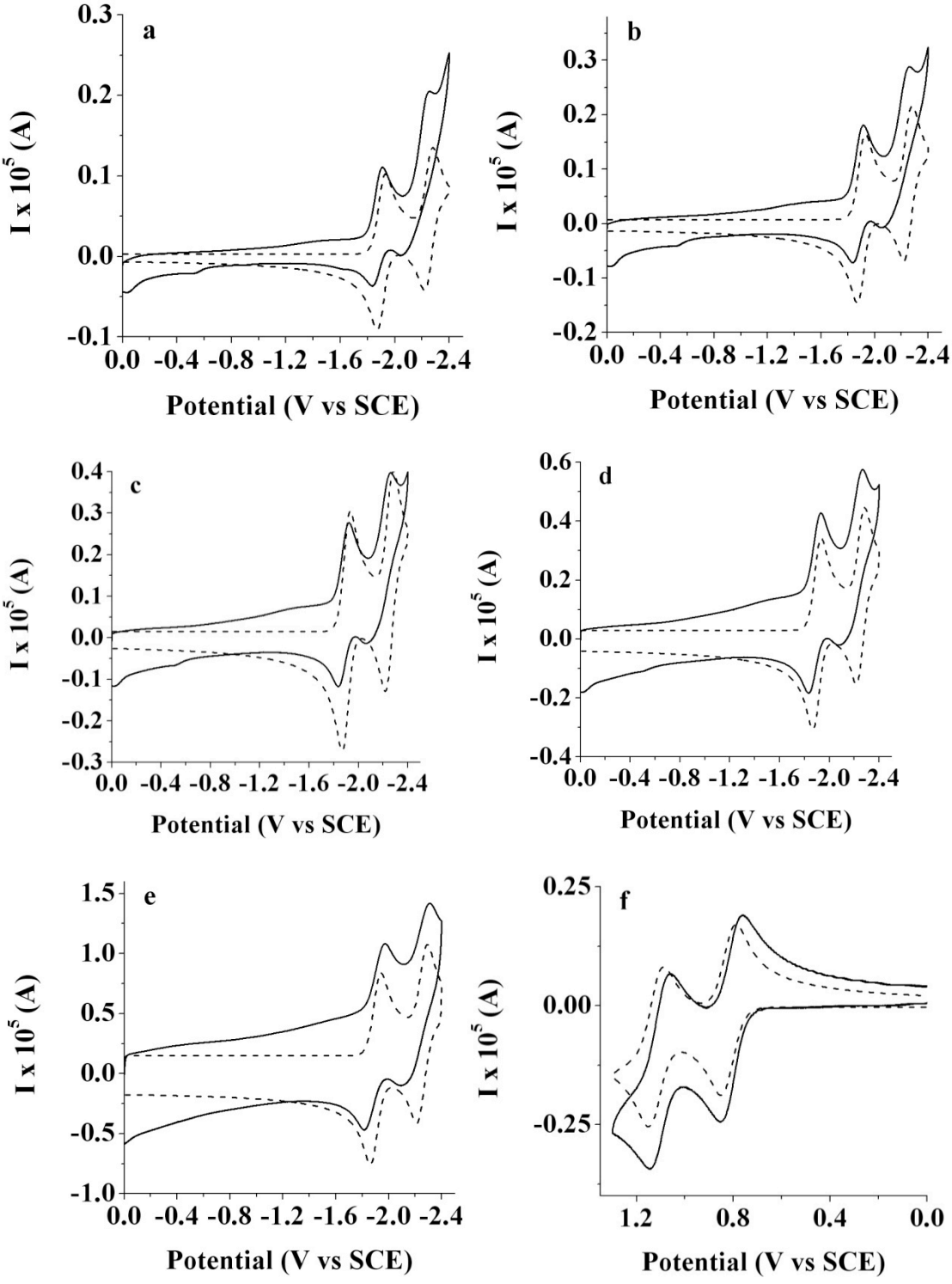
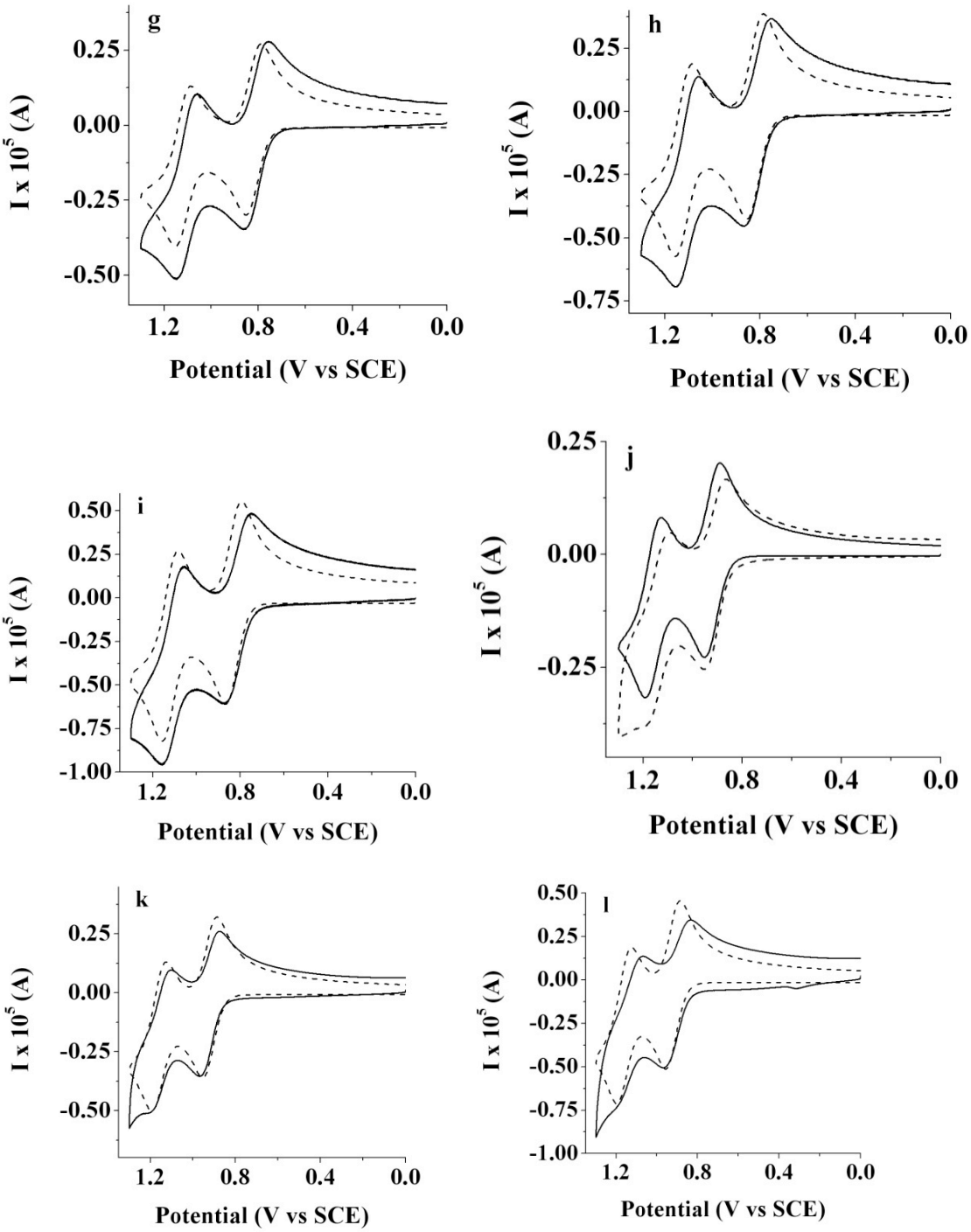


Figure S6. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.6 mM **t-trimer-2** during the scan in the negative direction (a)-(h) and 1.9 mM **t-trimer-2** during scan in the positive direction (i)-(n). Scan rates for reduction (a) 1 V/s; (b) 2 V/s; (c) 3 V/s; (d) 5 V/s; (e) 0.1 V/s; (f) 0.25 V/s; (g) 0.5 V/s; (h) 1 V/s; scan rates for oxidation: (i) 0.1 V/s; (j) 0.25 V/s; (k) 0.5 V/s; (l) 1 V/s; (m) 5 V/s; (n) 10 V/s. Experimental data: solvent: (a)-(d) THF, (e)-(n) 1:1 benzene: acetonitrile; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 6.6 x 10^{-6} cm^2/s; uncompensated resistance: 1000 Ω; capacitance: 3 x 10^{-7} F.





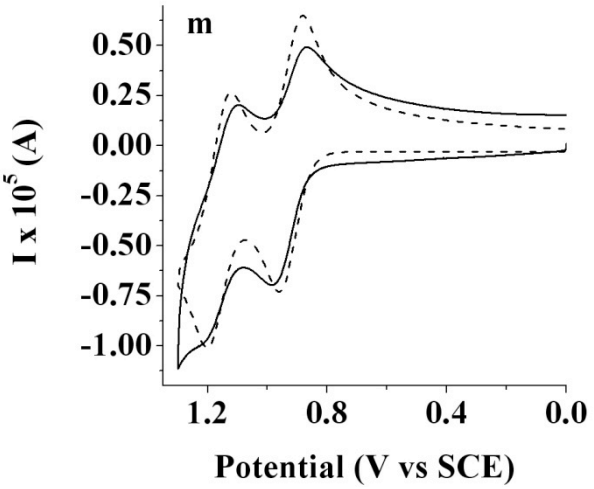
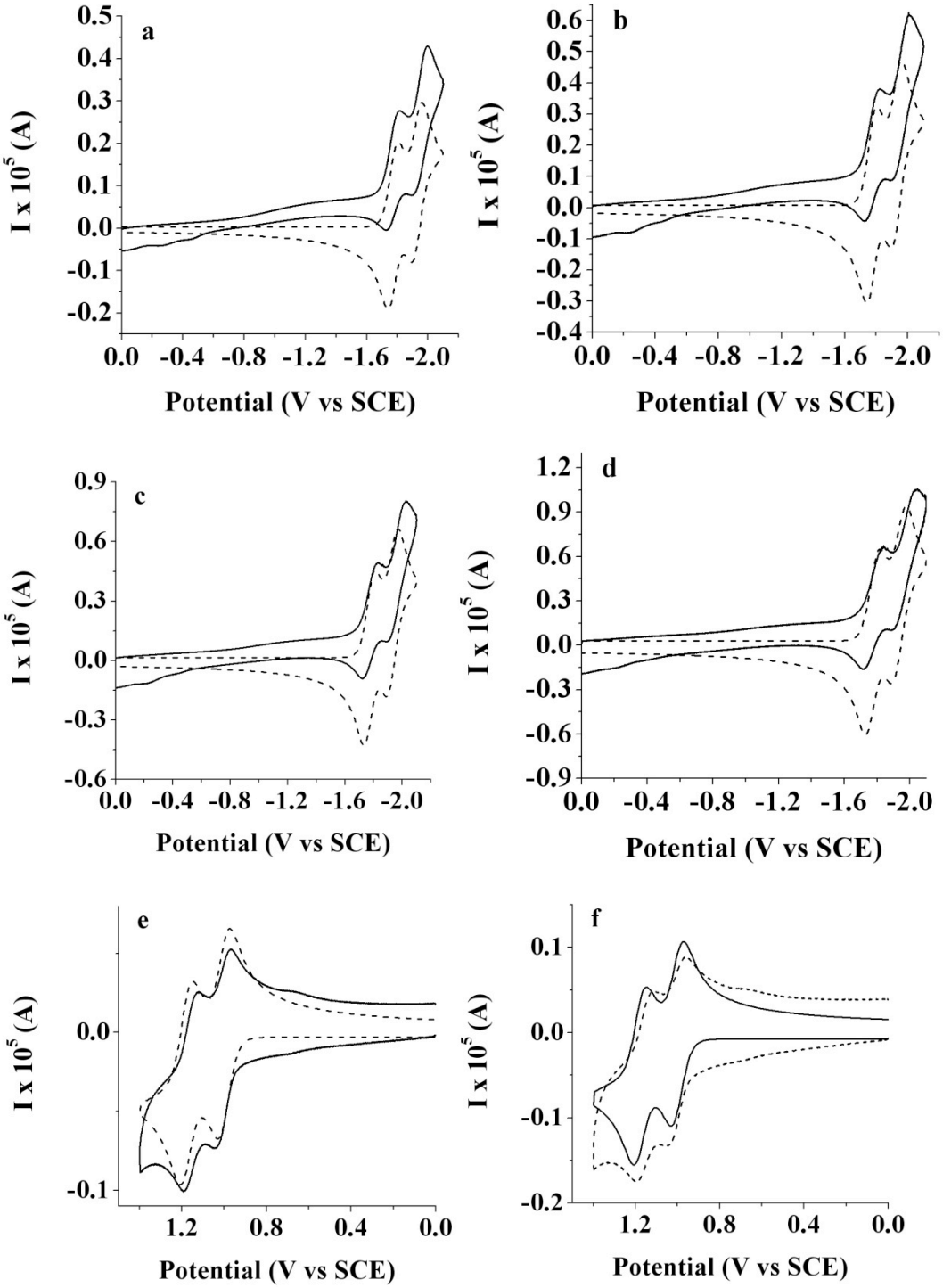


Figure S7. Experimental (solid) and simulated (dashed) line cyclic voltammograms of **t-tetramer** during the scan in the negative direction (a)-(e) and positive direction (f)-(m); concentrations used: (a)-(e) 0.15 mM; (g)-(i) 0.28 mM; (j)-(m) 0.34 mM; scan rates for reduction (a) 0.1 V/s; (b) 0.25 V/s; (c) 0.5 V/s; (d) 1 V/s; (e) 5 V/s; scan rates for oxidation (f) and (j) 0.1 V/s; (g) and (k) 0.25 V/s; (h) and (l) 0.5 V/s; (i) and (m) 1 V/s. Experimental data: solvent: (a)-(e) THF, (f)-(i) DCM, (j)-m) 1:1 benzene: acetonitrile; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 6.2 x 10^{-6} cm^2/s; uncompensated resistance: 1000 Ω; capacitance: 3 x 10^{-7} F.



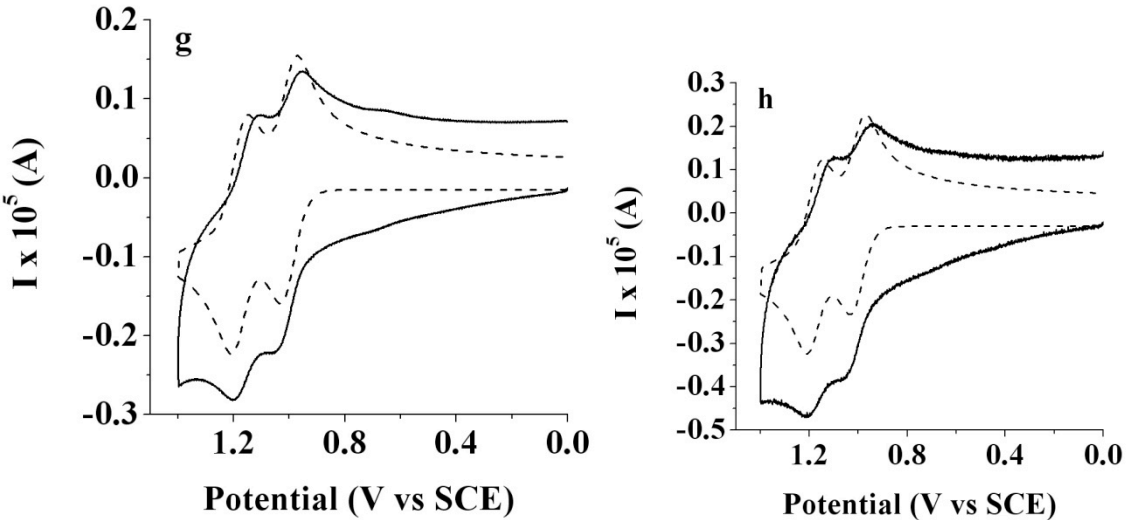


Figure S8. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.3 mM **t-hexamer-3** during the scan in the negative direction (a)-(d) and 0.15 mM **t-hexamer-3** (e)-(h) in the positive direction. Scan rates for reduction (a) 0.1 V/s; (b) 0.25 V/s; (c) 0.5 V/s; (d) 1 V/s. Experimental data: solvent: (a)-(d) THF, (e)-(h) 1:1 benzene: acetonitrile; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 6.2 x 10^{-6} cm^2/s; uncompensated resistance: 1200 Ω; capacitance: 3 x 10^{-7} F.

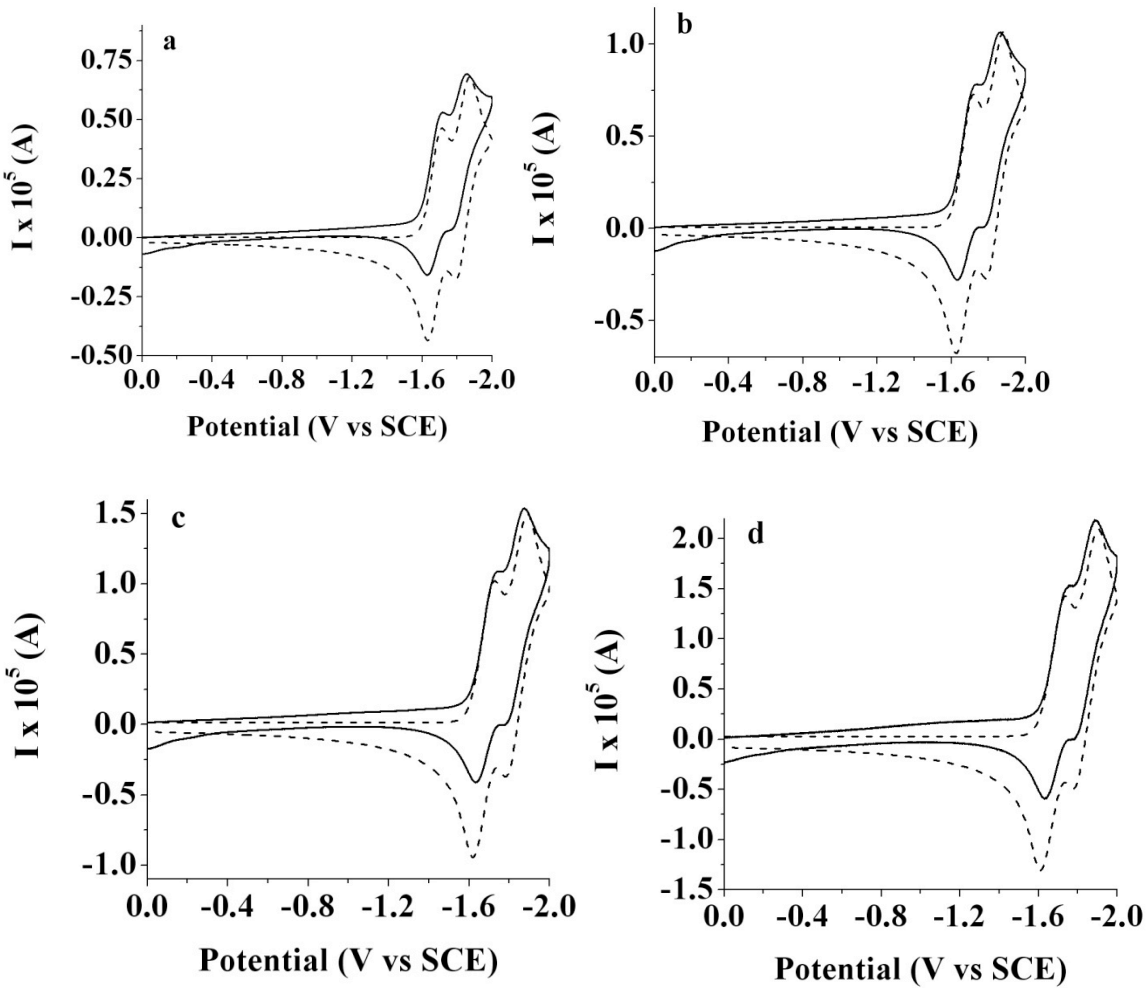


Figure S9. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.7 mM **t-hexamer-2** during the scan in the negative direction (a)-(d) Scan rates (a) 0.1 V/s V/s; (b) 0.25 V/s; (c) 0.5 V/s; (d) 1 V/s. Experimental data: solvent: THF; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 6.2 x 10^{-6} cm^2/s; uncompensated resistance: 1200 Ω; capacitance: 3 x 10^{-7} F.

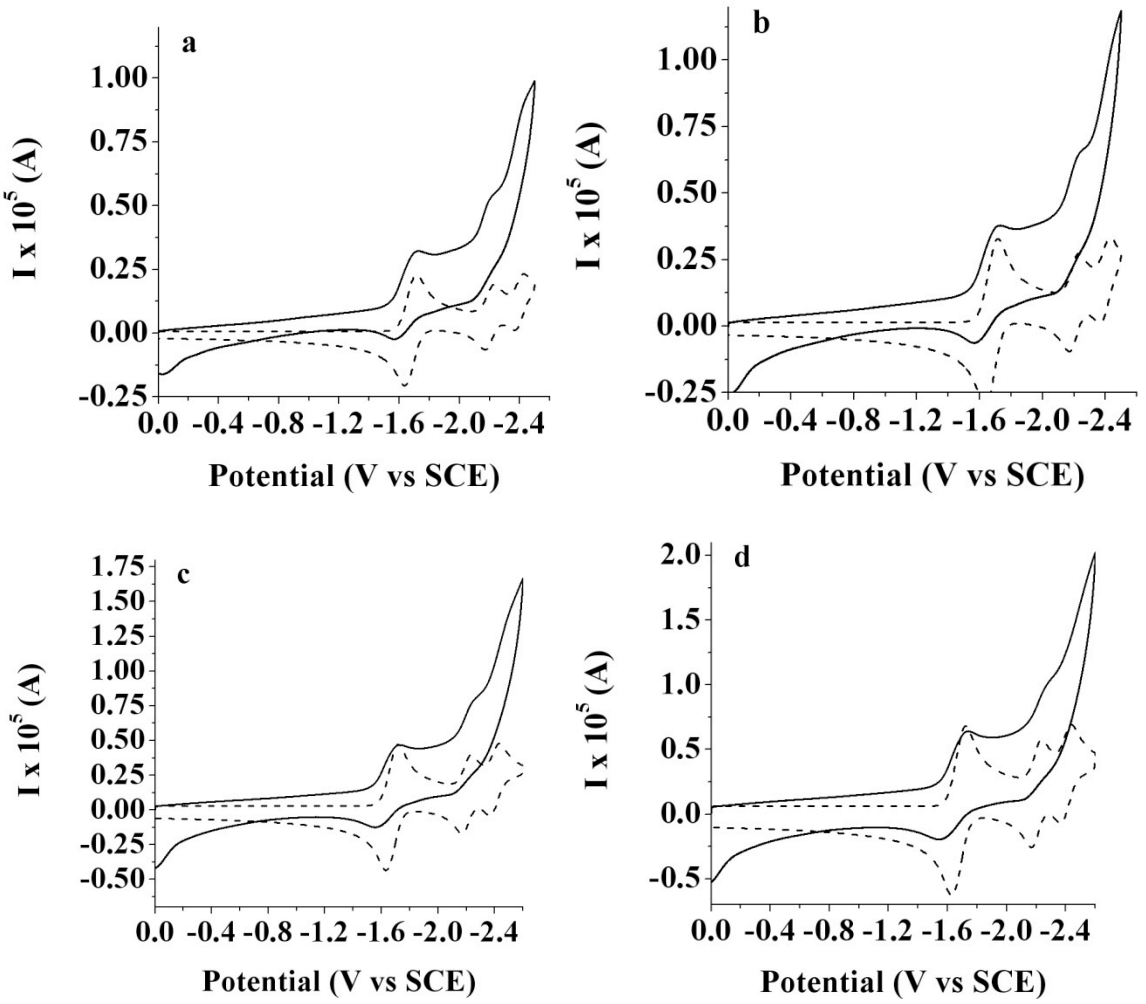


Figure S10. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.18 mM **t-octamer** during the scan in the negative direction (a)-(d) Scan rates (a) 0.25 V/s; (b) 0.5 V/s; (c) 1 V/s; (d) 2 V/s. Experimental data: solvent: THF; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 5.5 x 10^{-6} cm^2/s; uncompensated resistance: 1200 Ω; capacitance: 3 x 10^{-7} F.

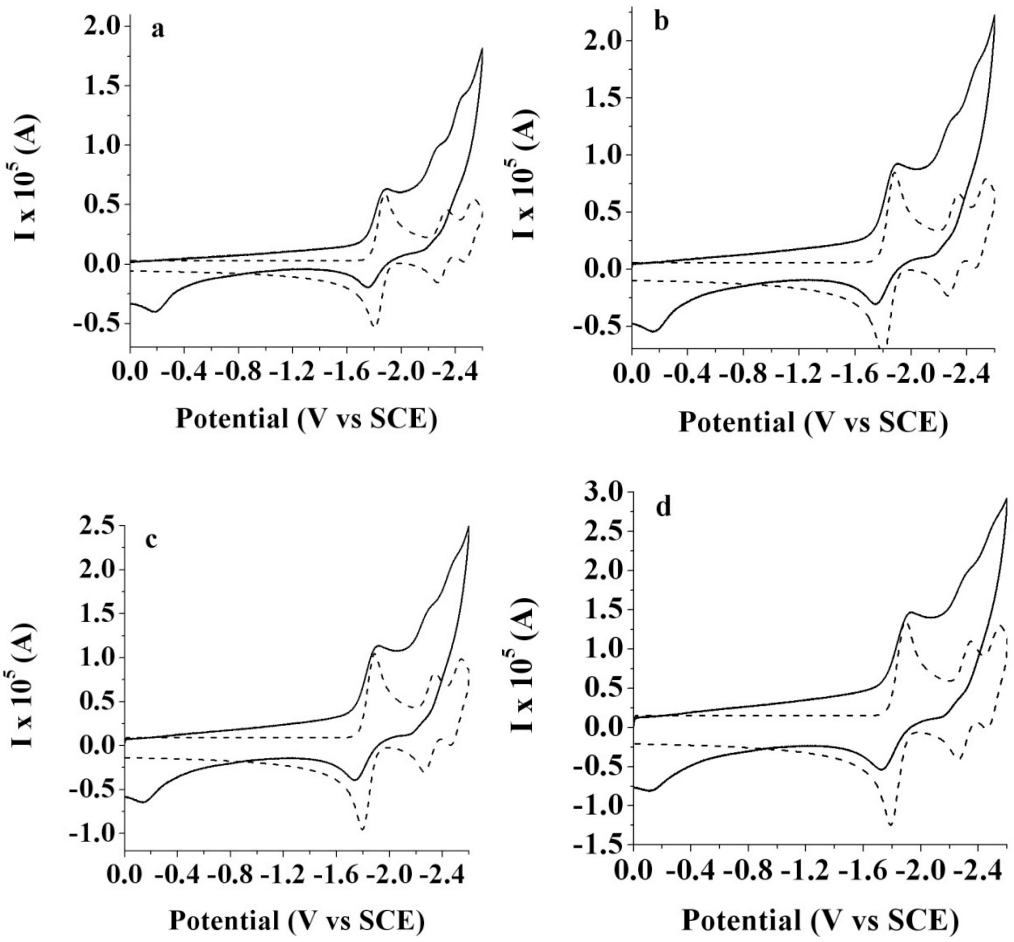


Figure S11. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.4 mM **t-nonamer** during the scan in the negative direction (a)-(d) Scan rates (a) 1 V/s; (b) 2 V/s; (c) 3 V/s; (d) 5 V/s. Experimental data: solvent: THF; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 5.3 x 10^{-6} cm^2/s; uncompensated resistance: 1200 Ω; capacitance: 3 x 10^{-7} F.

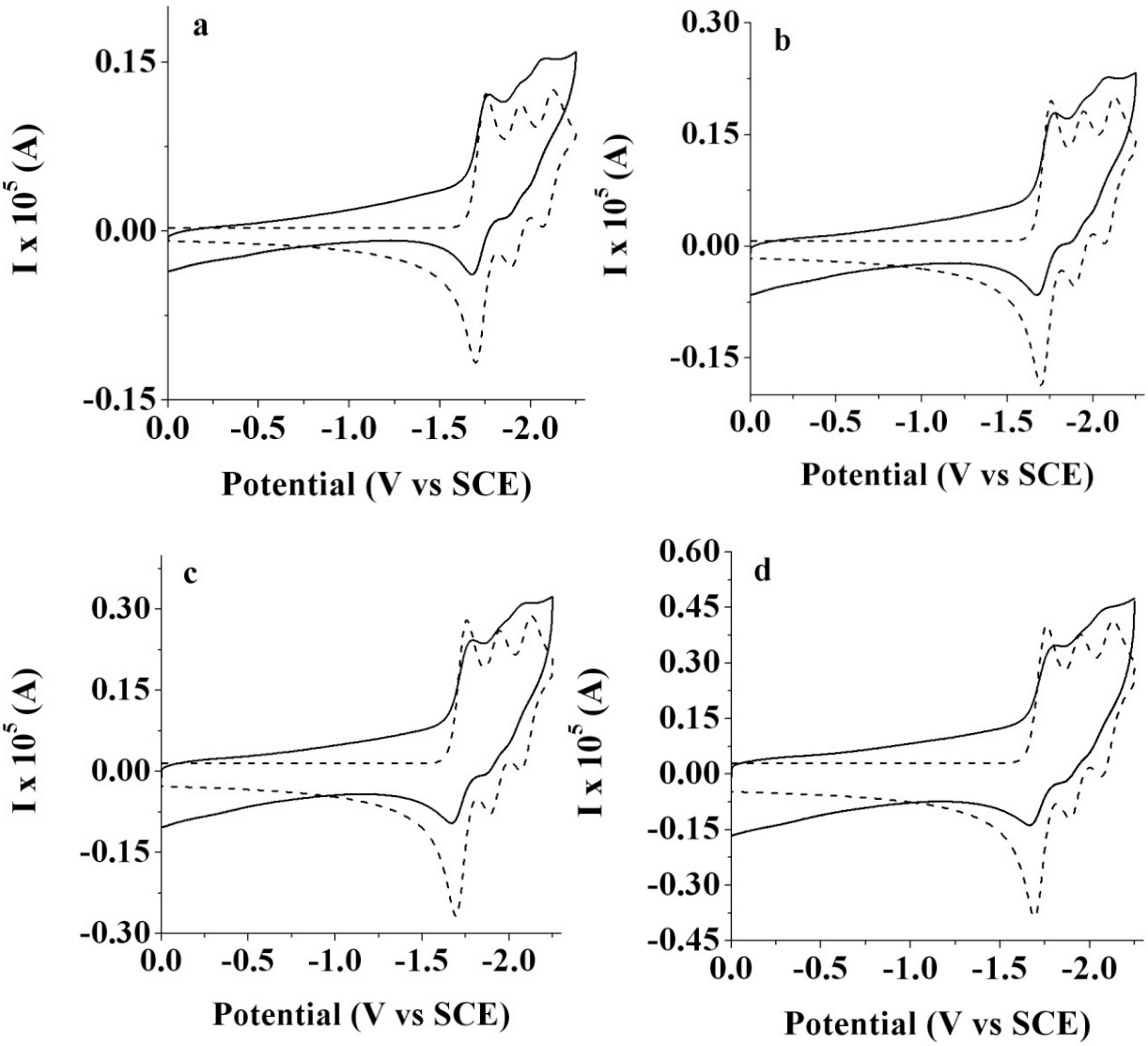
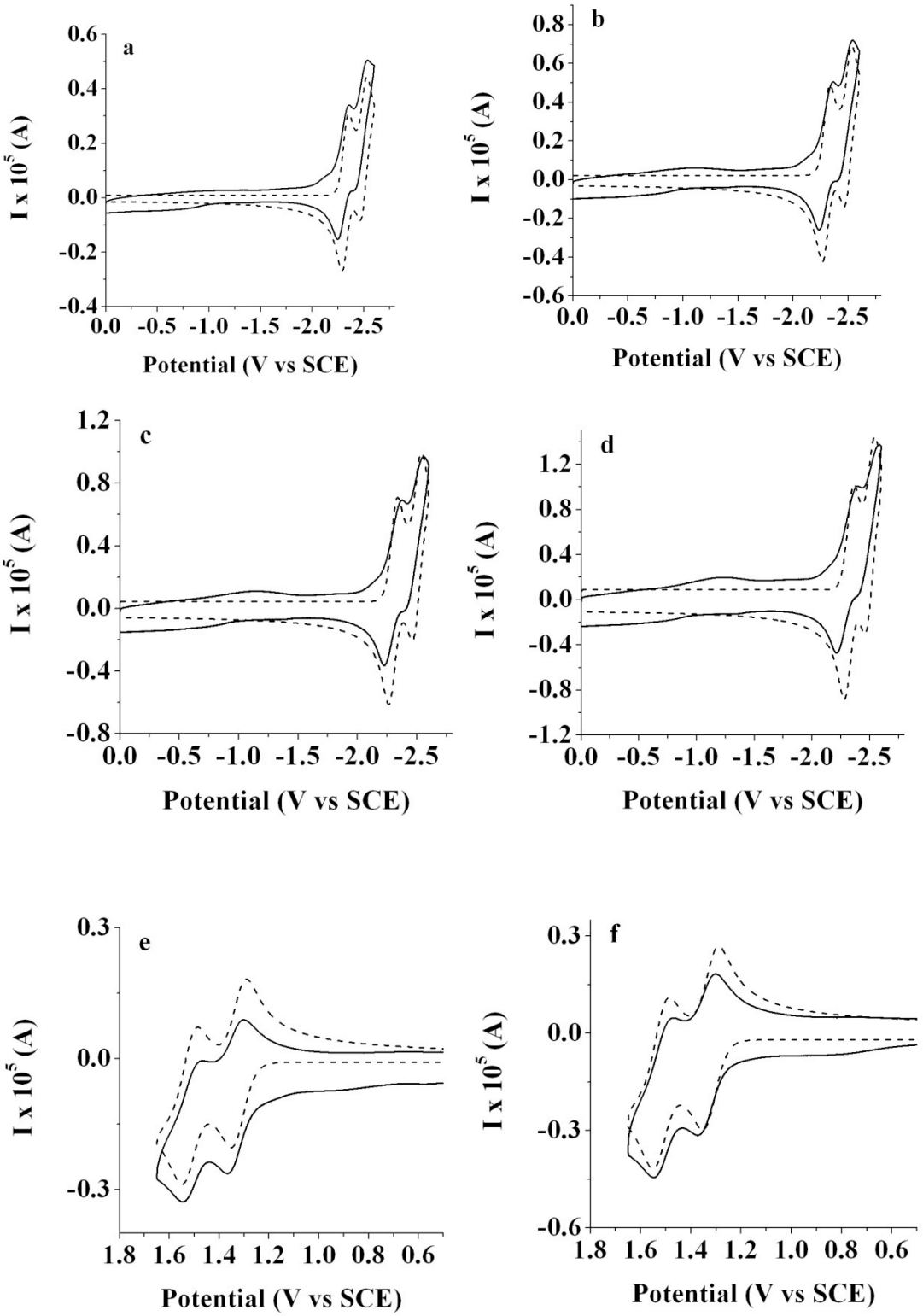


Figure S12. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.15 mM **t-dodecamer** during the scan in the negative direction (a)-(d); (a) 0.1 V/s; (b) 0.25 V/s; (c) 0.5 V/s; (d) 1 V/s; solvent: THF; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 4.8 x 10^{-6} cm^2/s; uncompensated resistance: 1000 Ω; capacitance 3 x 10^{-7} F.



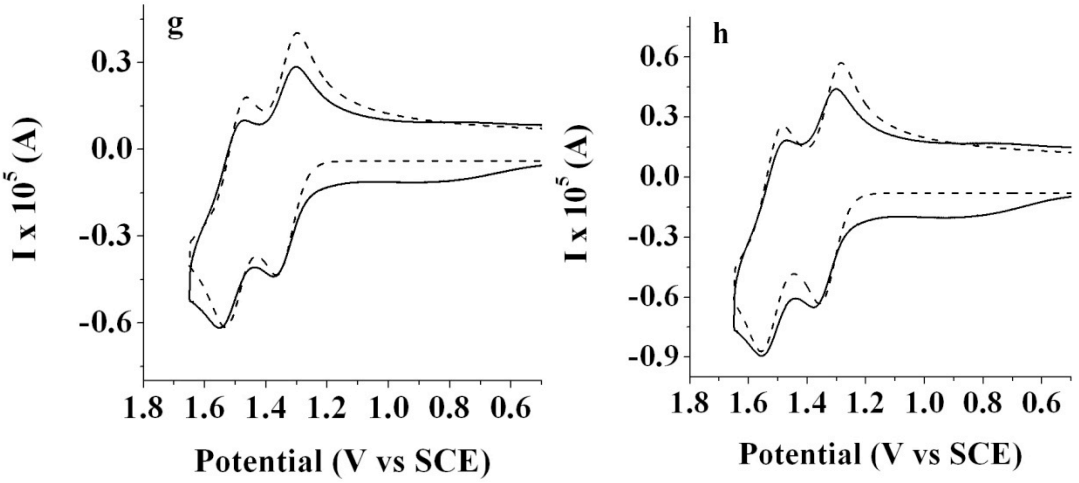
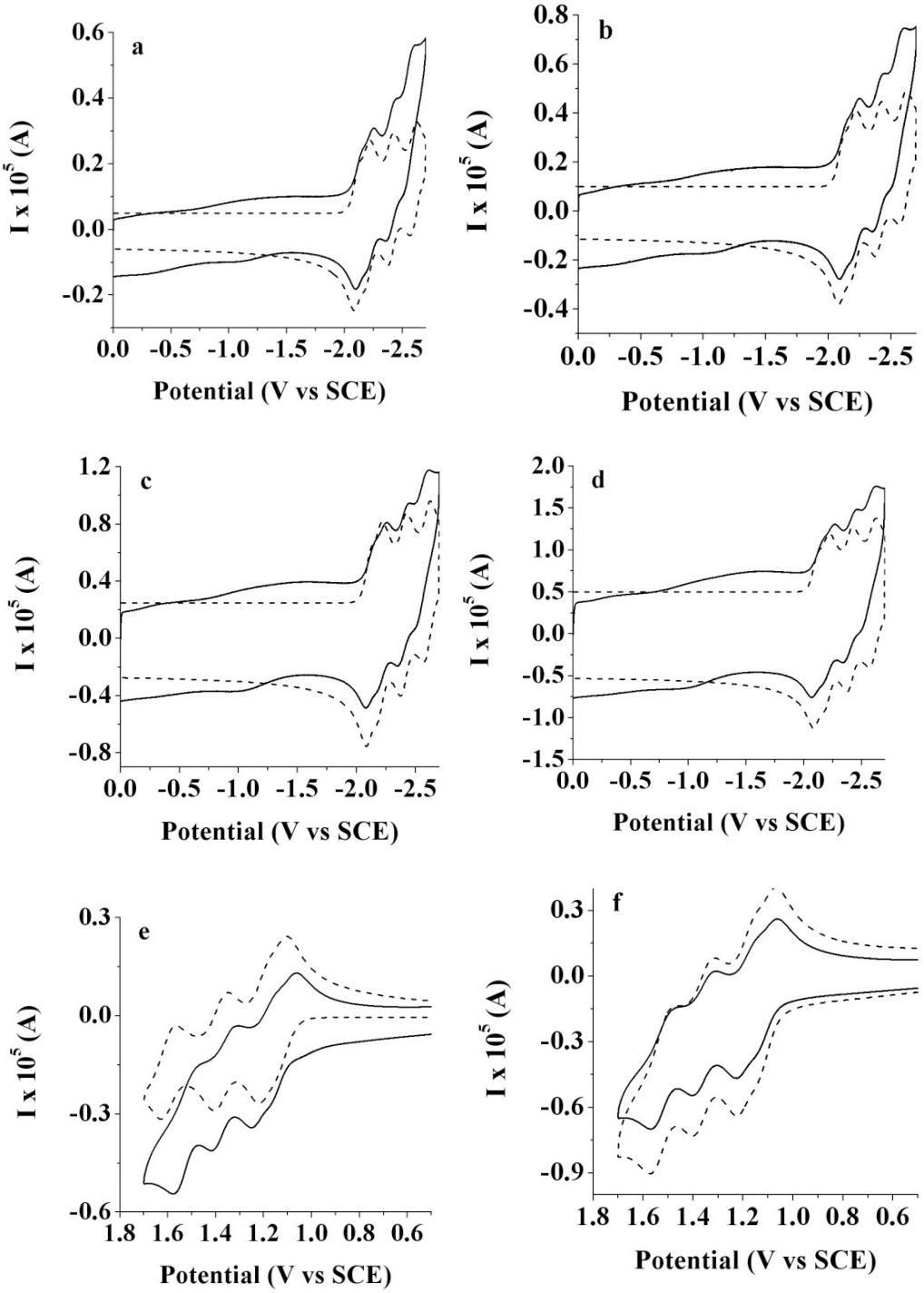


Figure S13. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.3 mM **f-trimer** during the scan in the negative direction (a)-(d) and positive direction (e)-(h). Scan rates for reduction (a) 0.1 V/s; (b) 0.25 V/s; (c) 0.5 V/s; (d) 1 V/s; Scan rates for oxidation (f) 0.1 V/s; (g) 0.25 V/s; (h) 0.5 V/s; (i) 1 V/s. Experimental data: solvent: (a)-(d) THF; (e)-(h) 1:1 benzene-acetonitrile; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2; Simulated data: diffusion coefficient: 6 x 10^{-6} cm^2/s; uncompensated resistance: 1000 Ω; capacitance 3 x 10^{-7} F.



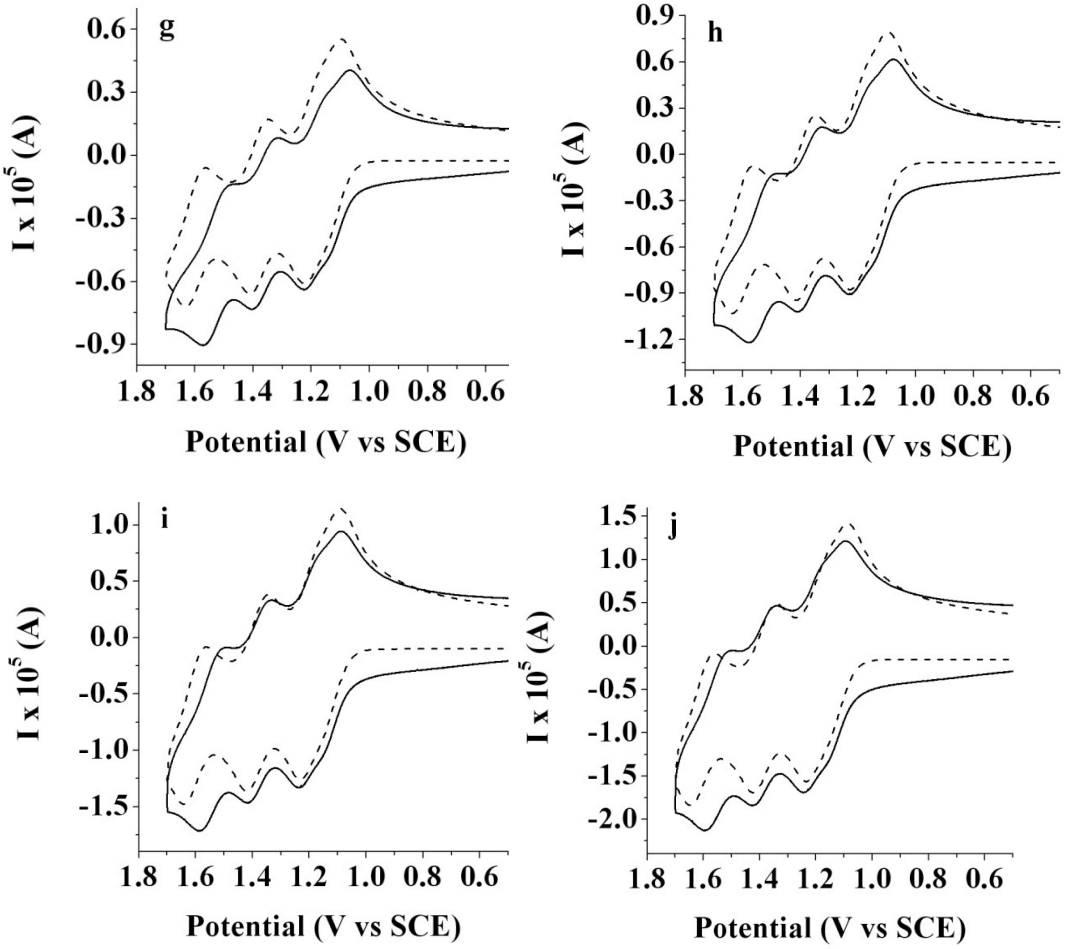
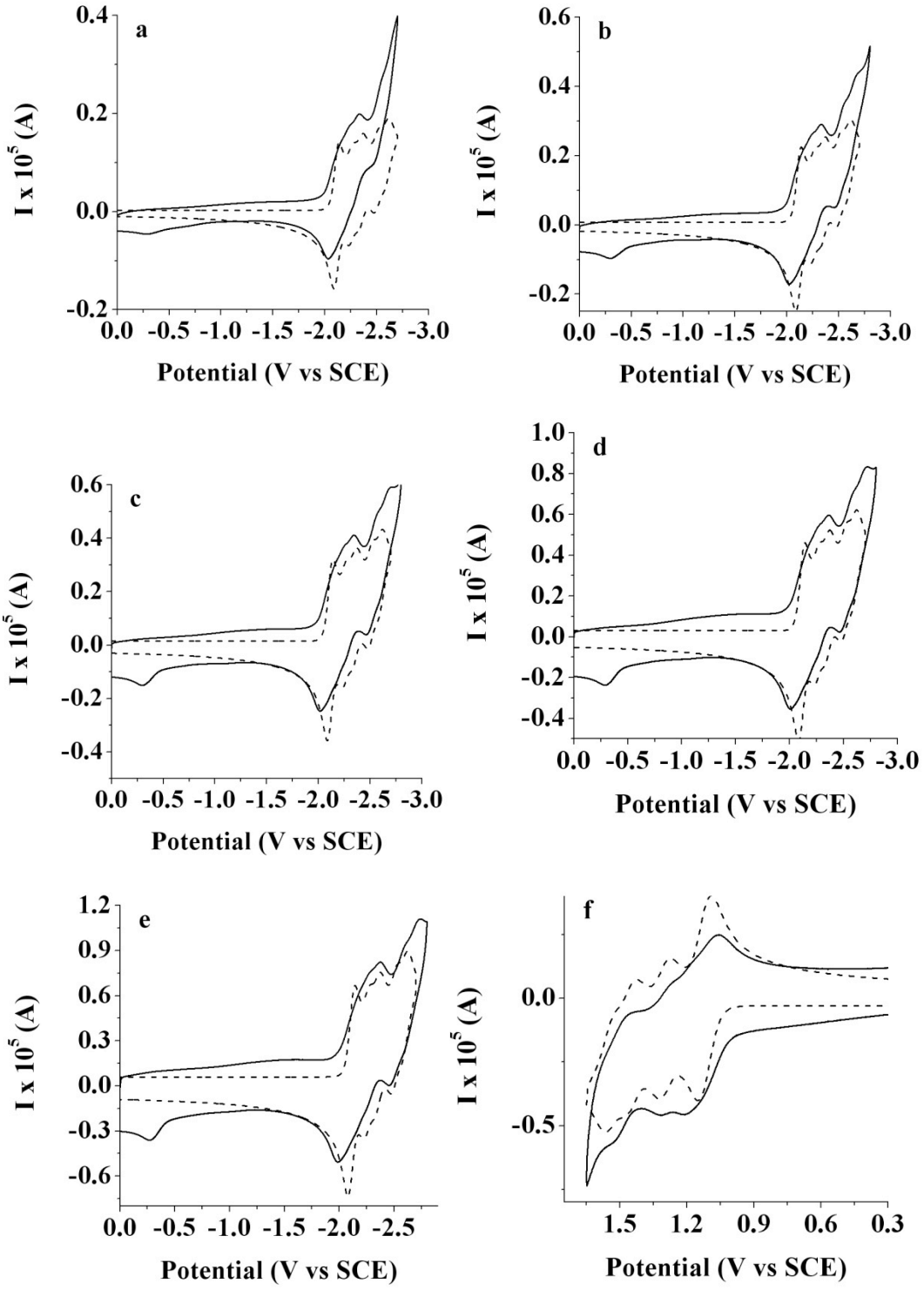


Figure S14. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.08 mM **f-pentamer** during the scan in the negative direction (a)-(d) and 0.25 mM **f-pentamer** during the scan in the positive direction (e)-(j). Scan rates for reduction: (a) 1 V/s; (b) 2 V/s; (c) 5 V/s; (d) 10 V/s; Scan rates for oxidation: (e) 0.1 V/s; (f) 0.25 V/s; (g) 0.5 V/s; (h) 1 V/s; (i) 2 V/s; (j) 3 V/s. Experimental data: solvent: (a)-(d) THF, (e)-(j) 1:1 benzene: acetonitrile; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2. Simulated data: diffusion coefficient: 5.4 x 10^{-6} cm^2/s; uncompensated resistance: 1000 Ω; capacitance: 3 x 10^{-7} F.



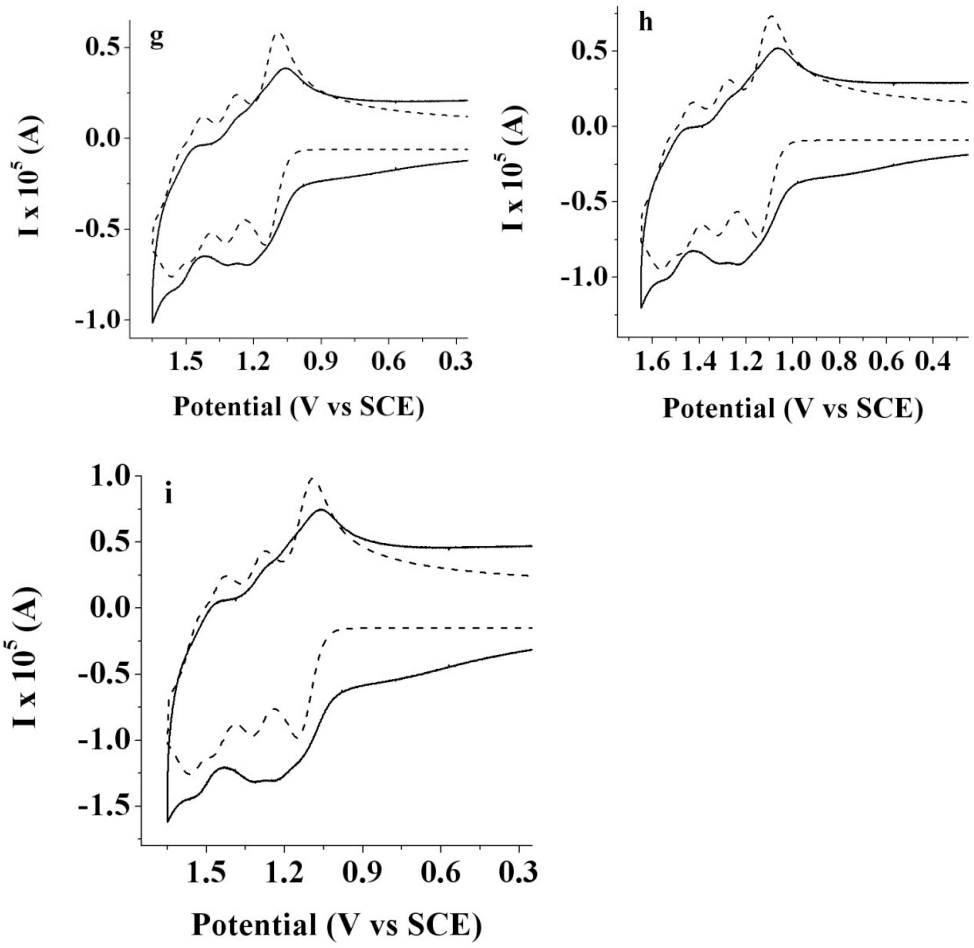


Figure S15. Experimental (solid) and simulated (dashed) line cyclic voltammograms of 0.14 mM **f-heptamer** during the scan in the negative direction (a)-(e) and positive direction (f)-(i). Scan rates for reduction (a) 0.1 V/s; (b) 0.25 V/s; (c) 0.5 V/s; (d) 1 V/s; (e) 2 V/s; Scan rates for oxidation: (f) 1 V/s; (g) 2 V/s; (h) 3 V/s; (i) 5 V/s. Experimental data: solvent: (a)-(e) THF, (f)-(i) 1:1 benzene: acetonitrile; 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: 1000 Ω; capacitance 3 x 10^{-7} F.

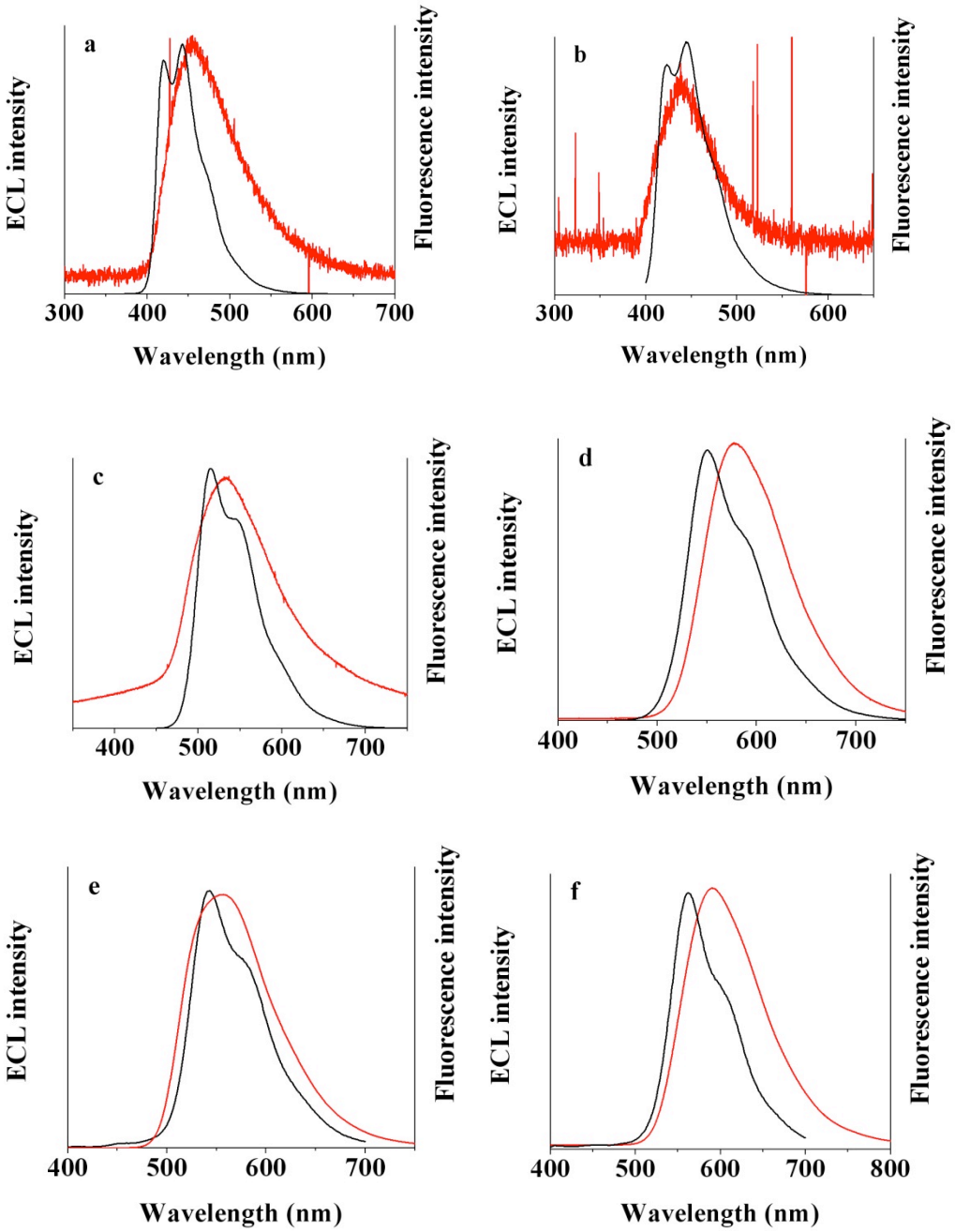


Figure S16. Electrogenerated chemiluminescence spectra of (a) 0.25 mM **t-trimer-1**; (b) 0.3 mM **t-trimer-2**; (c) 0.15 mM **t-hexamer-2**; (d) 0.1 mM **t-octamer**; (e) 0.1 mM **t-nonamer**; (f) 0.1 mM **t-dodecamer**; spectra (a) and (b) were obtained by annihilation from 80 mV from the first peaks. All other spectra were obtained by using 10 mM benzoyl peroxide and applying potential 80 mV negative from the first reduction wave; supporting electrolyte: 0.1 M $TBAPF_6$; platinum electrode area: 0.0314 cm^2; frequency of pulsing 10 Hz.