Supporting Information

Electrochemistry, ECL and Excimer Formation Dynamics of Intramolecular π-stacked 9-

Naphthylanthracene Derivatives and Organic Nanoparticles

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Figure S1. Reduction CV (blue line) of 0.5 mM solutions of **4A** in BZN with background CV (red line). WE: Pt disk, CE: Pt coil, RE: Ag wire as a QRE. Scan rate was 0.5 V/s.



Figure S2. (a) Cyclic voltammogram of 0.5 mM **4A**. Scan rate was 0.05 V/s. (b) Plot of the experimental ratio $i_d(t)/i_{d,ss}$ against the inverse square root of time for the oxidation of 0.5 mM

4A. Sampling ratio is 10 μ s per point. The result of the linear regression is shown together. Both were performed in DCM with 0.1 M TBAPF₆. WE: 25 μ m diameter Pt UME, CE: Pt coil, RE: Ag wire as a QRE.



Figure S3. Experimental (solid line) and simulated (dotted line) cyclic voltammograms of 0.5 mM 4A oxidation with scan rate from 50 mV/s to 10 V/s. Simulation mechanism is two, one-

electron oxidations and corrected for uncompensated resistance, R_u (3240 Ω) and double layer capacitance, C_d (500 nF): $E^{\circ}_{1,ox} = 1.22$ V, $E^{\circ}_{2,ox} = 1.25$ V vs. SCE, $k^{\circ} \ge 10^4$ cm/s, $\alpha = 0.5$.



Figure S4. Experimental (solid line) and simulated (dotted line) cyclic voltammograms of 0.4 mM **4C** oxidation with scan rate from 50 mV/s to 10 V/s. Simulation mechanism is three, one-electron oxidation and corrected for uncompensated resistance, R_u (2700 Ω) and double layer



capacitance, C_d (600 nF): $E^{\circ}_{1,ox} = 1.17$ V, $E^{\circ}_{2,ox} = 1.21$ V and $E^{\circ}_{3,ox} = 1.25$ V vs. SCE, $k^{\circ} \ge 10^4$ cm/s, $\alpha = 0.5$.

Figure S5. Experimental (solid line) and simulated (dotted line) cyclic voltammograms of 0.5 mM **4A** reduction with scan rate from 50 mV/s to 2 V/s. Simulation mechanism is two, one electron oxidation and corrected for uncompensated resistance, R_u (8092 Ω) and double layer capacitance, C_d (1000 nF): $E^{\circ}_{1,red} = -2.08$ V and $E^{\circ}_{2,red} = -2.13$ V vs. SCE, $k^{\circ} \ge 10^4$ cm/s, $\alpha = 0.5$.



Figure S6. Experimental (solid line) and simulated (dotted line) cyclic voltammograms of 0.5 mM **4C** reduction with scan rate from 50 mV/s to 2 V/s. Simulation mechanism is two, one electron oxidation and corrected for uncompensated resistance, R_u (6659 Ω) and double layer capacitance, C_d (400 nF): $E^{\circ}_{1,red} = -1.97$ V, $E^{\circ}_{2,red} = -2.02$ V and $E^{\circ}_{3,red} = -2.07$ V vs. SCE, $k^{\circ} \ge 10^4$ cm/s, $\alpha = 0.5$.



Figure S7. (a) CVs for oxidation of 0.5 mM solutions of **4A** in DCM at various scan rates. (b) Oxidation peak current versus the square root of the scan rate $(v^{1/2})$.



Figure S8. Film thickness dependence on the fluorescence intensity in solid state of (a) **4A** and (b) **4C**.



Figure S9. (a) CVs of 0.5 mM 4C in BZN before and after ECL measurement (b) 1^{st} and 2^{nd} ECL spectrum of 4C.



Figure S10. Initial current (black) and ECL light (red) transients for compound 4C pulsed between and -1.96 V and + 1.44 V versus Ag quasi-reference electrode. Pulse width is (a) 0.1 s (b) 0.5 s.



Figure S11. ECL spectrum of 0.5 mM 4A without (black line) and with (red line) 50 mM TPrA as the co-reactant.