Supporting information

Electrochemical Controlling and Monitoring of Halogen Bond Formation in Solution.

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1) **Experimental conditions and procedures**
2) **Tables and Figures based on experimental data**
3) **Simulations of the cyclic voltammograms**

1) Experimental conditions and procedures

All chemicals were purchased either from SIGMA-ALDRICH, ACROS, or TCI EUROPE and thoroughly dried prior to the experiments. The solids were dried at 50°C in vacuum. Acetonitrile was distilled over calcium hydride and toluene over sodium. All liquid substrates were filtered over activated alumium oxide. ^{1}H, ^{19}F and ^{13}C NMR spectra of the halo-perfluoro carbons were recorded on a Bruker AC 400 MHz in order to verify their purity. Cyclic voltammetry experiments were performed using a CHI 660D potentiostat (CH Instruments, Inc., USA). The measurements were performed in a standard one-compartment three electrode cell containing 0.1 M solution of $TBAPF_6$ in anhydrous acetonitrile thermostated at 25 °C. Mechanically polished glassy carbon disk electrodes (carbon rod of 3 mm diameter, embedded in an insoluble polymer matrix) were employed as working electrodes and a platinum wire as auxiliary electrode. A salt bridge containing the electrolyte was used to connect the electrochemical cell with a saturated calomel reference electrode (SCE).

General procedure for measurement of the formal standard potentials:

Electrolyte and solvent were added to the electrochemical cell equipped with working, reference and auxiliary electrode protected under anhydrous argon atmosphere. The solvent was degassed by purging with acetonitrile saturated argon for a few minutes. After taking a background scan, the quinone and internal reference were added and a cyclic voltammogram performed. The difference in the measured formal standard potentials of the second reduction wave of the quinone relative to the first reduction wave (and the internal standard) ΔE°' was then calculated.

2) Tables and Figures based on experimental data

Table S1. Cyclic voltammetry data of TCQ (0.5 mM) in the absence and the presence of compound **1** in 0.1 M $TBAPF_6$/acetonitrile on glassy carbon, vs. SCE, scan rate : 100 mV/s, T=25°C.

Conc. of **1**	Reduction step	E_{pc}[a] / mV	E_{pa}[b] / mV	ΔE_p[c] / mV	C_{pa}/C_{pc}[d]	$E^{\circ\prime}$ [e] / mV	$\lvert\Delta E^{\circ\prime}\rvert$ [f] / mV
0 mM	I^{st}	- 16	75	91	1.01	30	—
0 mM	II^{nd}	- 779	- 671	108	1.03	- 725	—
50 mM	I^{st}	- 18	75	93	0.97	29	**1**
50 mM	II^{nd}	- 645	- 525	129	0.92	- 590	**136**

[a] cathodic peak potential; [b] anodic peak potential; [c] $\Delta E_p = E_{pa} - E_{pc}$; [d] peak ratio; [e] $E^{\circ\prime} = (E_{pa}+E_{pc})/2$; [f] potential shift after addition of **1**.

Table S2. Apparent formal half wave potential shifts ΔE°' of the 2nd reduction wave of TCQ (0.5 mM) upon addition of 100 equivalents (50 mM) of aliphatic substrates in 0.1 M TBAPF$_6$ in acetonitrile at 25°C.

perfluorinated substrates	Δ E°' / mV	non fluorinated substrates	Δ E°' / mV
C_6F_{13}-I (**1**)	141	C_6H_{13}-I	26
C_6F_{13}-Br	35	C_6H_{13}-Br	27
C_6F_{13}-F	— [a]	C_6H_{13}-Cl	19
C_4F_9-I (**2**)	140 [b]	*n*-hexane	26
		ethanol	53

[a] The solubility of perfluoro-*n*-hexane in the electrolyte was found to be below 10 mM, [b] partial loss of reversibility of the 2nd reduction wave at substrate concentration above 25 mM.

Table S3. Apparent formal half wave potential shifts ΔE°' of the 2nd reduction wave of TCQ (0.5 mM) upon addition of 100 equivalents (50 mM) of aromatic substrates in 0.1 M TBAPF$_6$ in acetonitrile at 25°C.

perfluorinated substrates	Δ E°' / mV	non fluorinated substrates	Δ E°' / mV
C_6F_5-I (**3**)	108	Ph-I	19
C_6F_5-Br	42	Ph-Br	11
C_6F_5-Cl	33	Ph-Cl	12
C_6F_5-F	33	benzene	20
C_6F_5-H	20		
p-$C_6F_4I_2$ (**4**)	100		

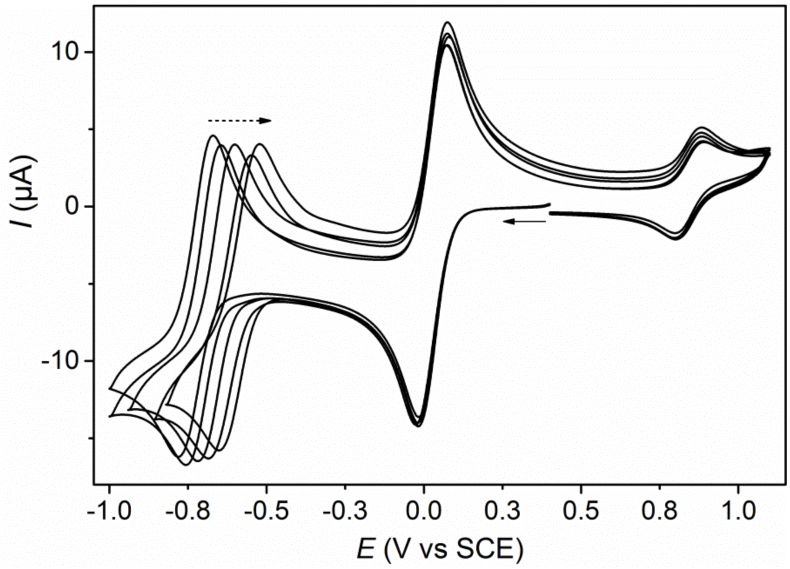

Figure S1. Cyclic voltamograms of TCQ (0.5 mM) and Os(bpy)$_3$PF$_6$ (0.12 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in acetonitrile in the absence and in the presence of increasing concentrations of iodo-perfluorohexane (**1**) (from left to right: 0, 0.5, 5, 25, 50 mM). Scan rate 0.1 V/s.

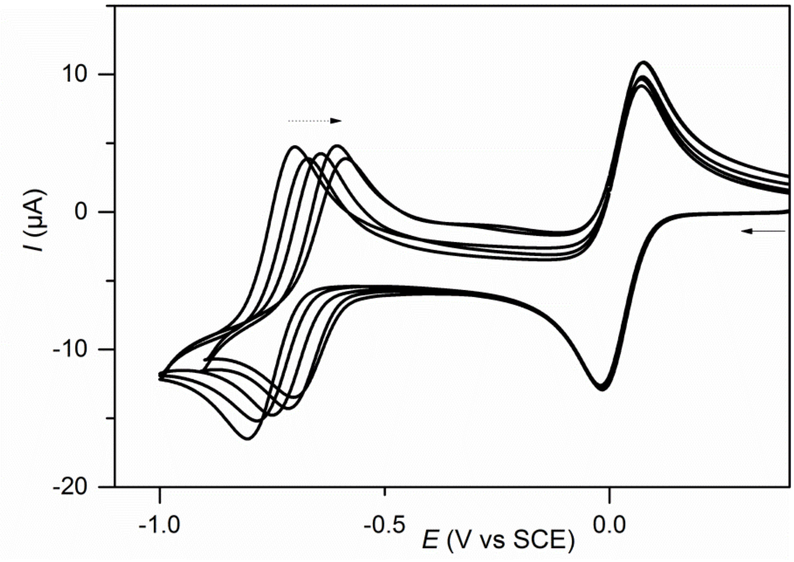

Figure S2. Cyclic voltamograms of TCQ (0.5 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in acetonitrile in the absence and in the presence of increasing iodo-perfluorobenzene (**3**) concentrations (from left to right: 0; 0.5, 5, 25; 50 mM). Scan rate 0.1 V/s.

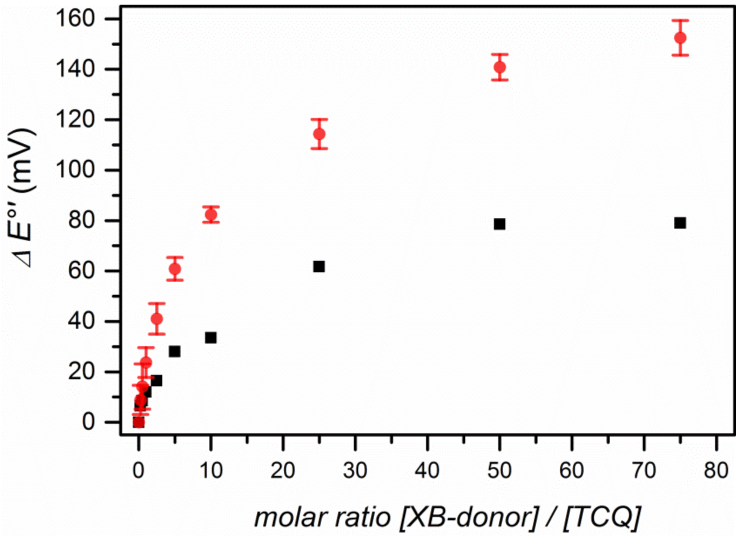

Figure S3. Dependence of the potential shift ΔE°' corresponding to the second reduction step of TCQ at 0.5 mM (red dots, including standard deviations) and 0.1 mM (black squares) on the concentration of the XB-donor **1** at 298 K.

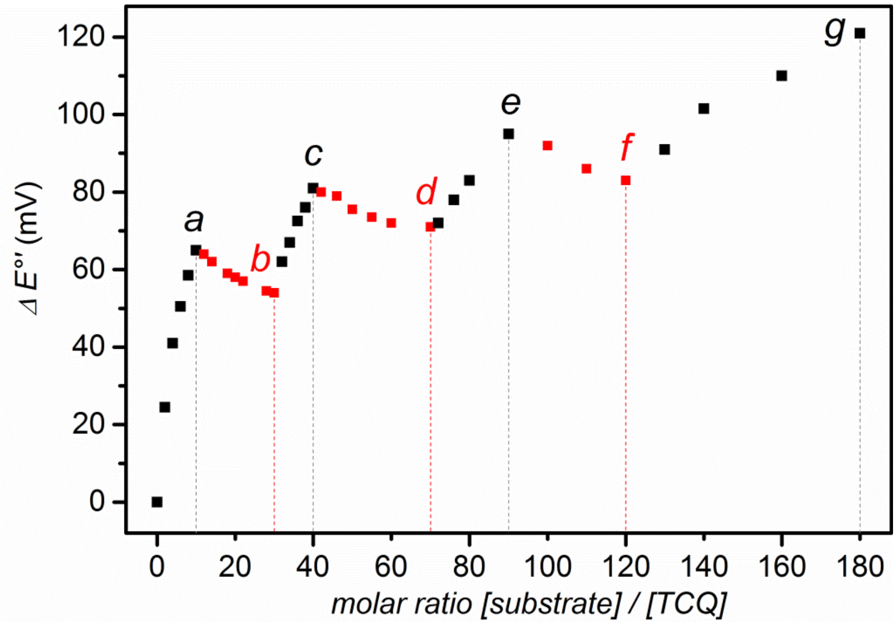

Figure S4. Potential shift of the second voltammetric wave of TCQ (0.5 mM) in a solution of 0.1 M TBAPF$_6$ in acetonitrile before and after adding successively the XB-donor **1** (black squares; *a*: 10 eq., *c*: 10 eq., *e*: 20 eq., *g*: 60 eq.) and the Lewis base Cl$^-$ in the form of TBACl (red squares; *b*: 20 eq., *d*: 30 eq., *f*: 30 eq.).

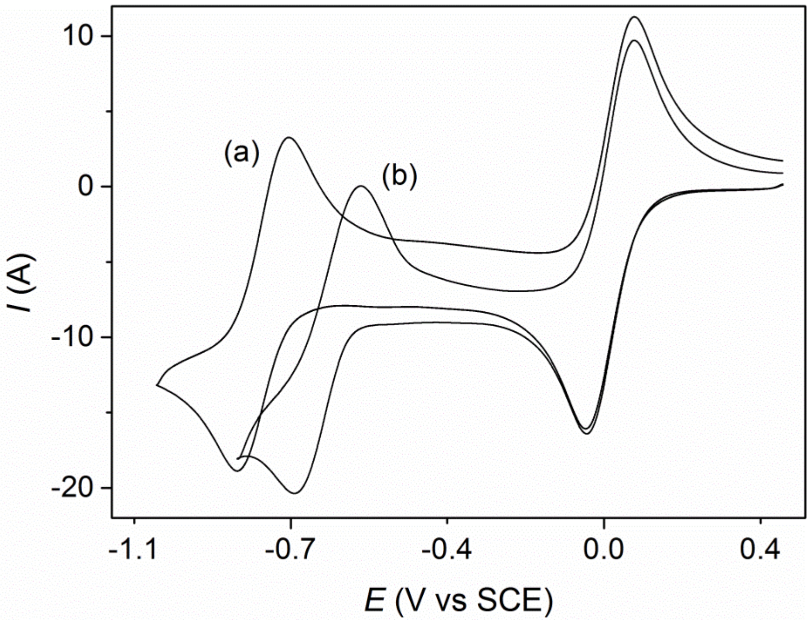

Figure S5. Cyclic voltamograms of TCQ (0.5 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ at 0.02M in acetonitrile in the absence (a) and in the presence (b) of 100 equivalents of iodo-perfluorohexane (**1**) concentrations. Scan rate 0.1 V/s.

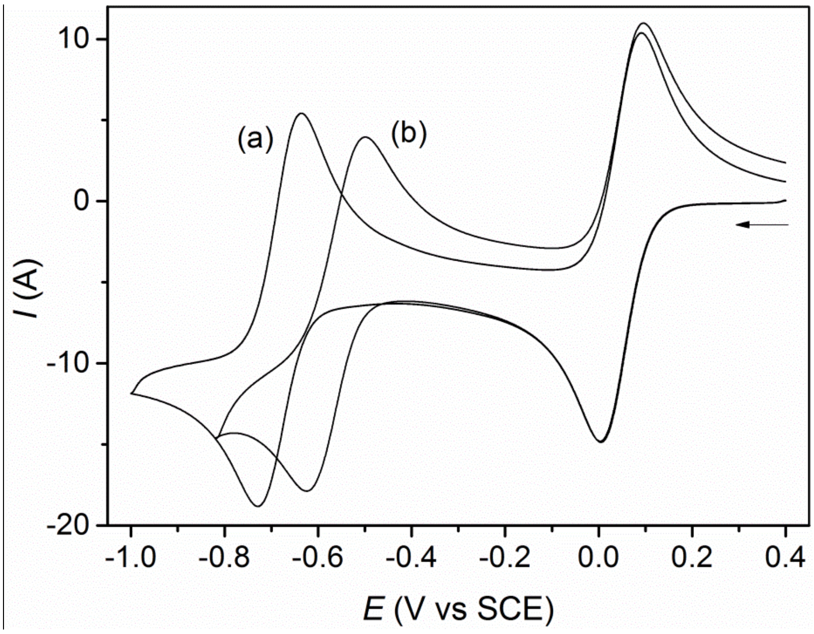

Figure S6. Cyclic voltamograms of TCQ (0.5 mM) on a glassy carbon electrode in a solution of tetramethylammonium hexafluorophosphate at 0.1 M in acetonitrile in the absence (a) and in the presence (b) of 100 equiv.of iodo-perfluorohexane (**1**) concentrations. Scan rate 0.1 V/s.

3) Simulations of the cyclic voltammograms

DigiElch v 7.F(SP) software (Bioanalytical Systems) was used to simulate the CVs and calculate the binding constants of TCQ with the XB donors iodo-perfluorohexane (**1**) and iodo-perfluorobenzene (**3**). Background subtracted CVs of TCQ in the absence and the presence of XB donor were fit to the square-scheme (Scheme 2 in the main text) considering only the formation of 1:1 complexes. The diffusion coefficient of TCQ was determined experimentally by cyclic voltammetry. The determined value of 1.77×10^{-5} cm^2/s is in agreement with literature values (1.5×10^{-5} and 1.8×10^{-5} cm^2/s).[1] It was found that the estimated diffusion coefficients of radical ions such as TCQ$^{\bullet-}$ (2.1×10^{-5} cm^2/s)[ref-1] in acetonitrile are very close to those of the parent neutral molecules suggesting relatively weak interactions between the charge delocalized ions and the solvent molecules. We used this value for both ions TCQ$^{\bullet-}$ and TCQ^{2-}. The diffusion coefficients of the XB donors were set at 1.8×10^{-5} cm^2/s and those of the corresponding XB complexes at 1×10^{-5} cm^2/s. Based on the hypothesis of extremely fast and exclusively diffusion controlled XB formations the corresponding rate constants k_{on} ($=k_f$) were set at 10^{10} M^{-1}s^{-1} (however smaller values of k_{on} in the range of 10^6-10^{10} M^{-1}s^{-1} did not significantly modify the final results). The heterogeneous electron-transfer rate constant k_s was determined by fitting the CVs in the absence of XB donors assuming a coefficient α of 0.5 and semi-infinite diffusion. The extracted value k_s (0.01 cm/s) was then used to fit the CVs in the presence of an XB donor by adjusting K_a^2 and K_a^3 to give the best fit to the experimental CVs.

[ref-1] R.L. Wang, K.Y. Tam, R.G. Compton, *J. Electroanal. Chem.* **1997**, *434*, 105-114.

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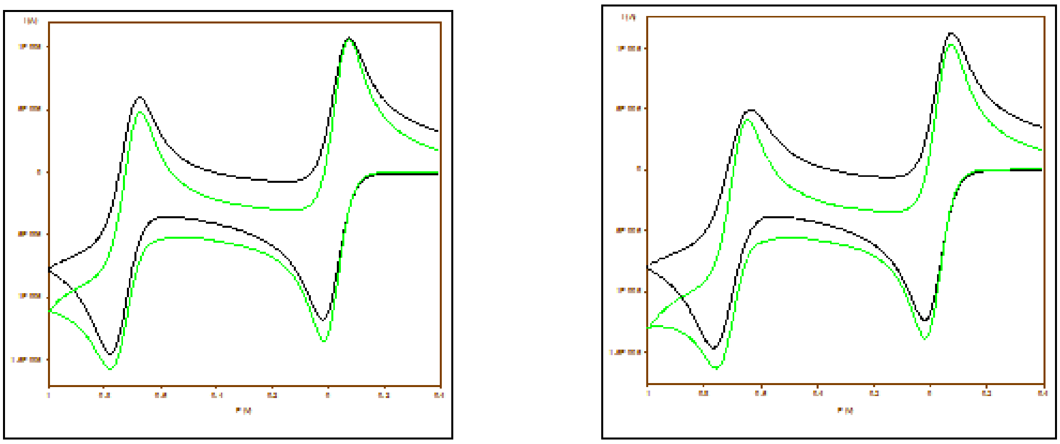
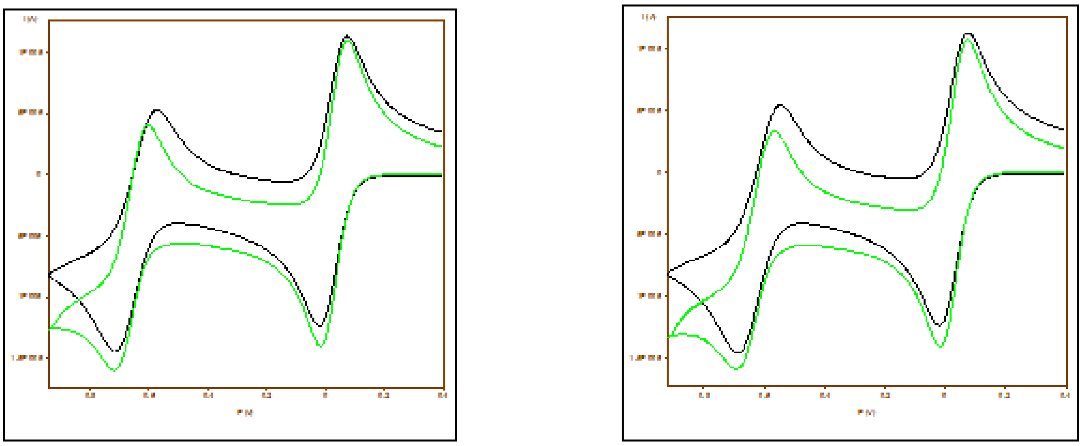
[1]



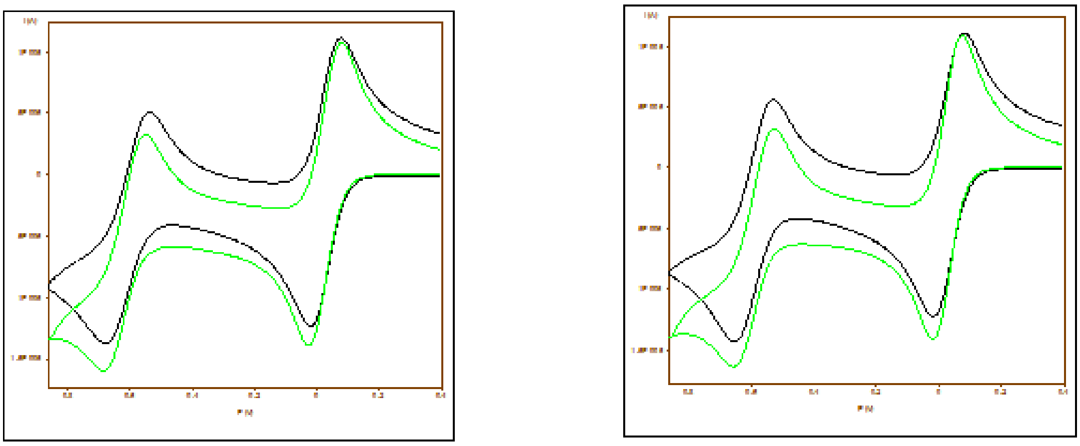
absence of **1**

1 equiv. of **1**



10 equiv. of **1**

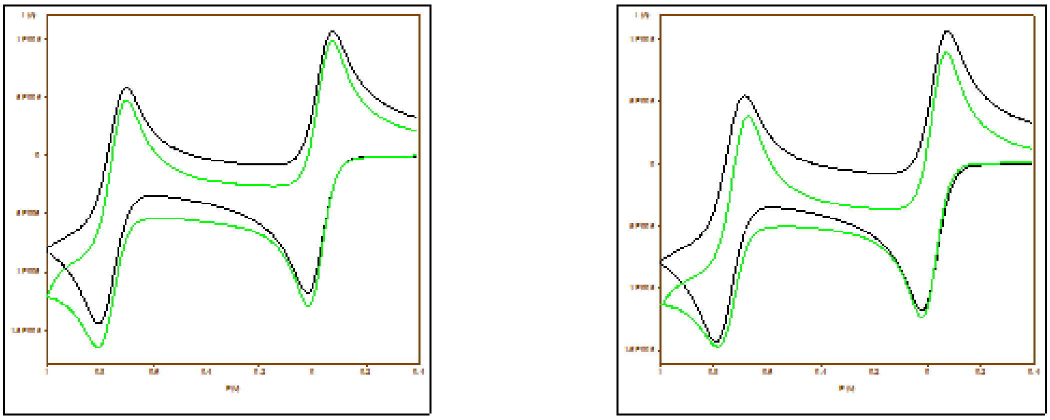
30 equiv. of **1**



50 equiv. of **1**

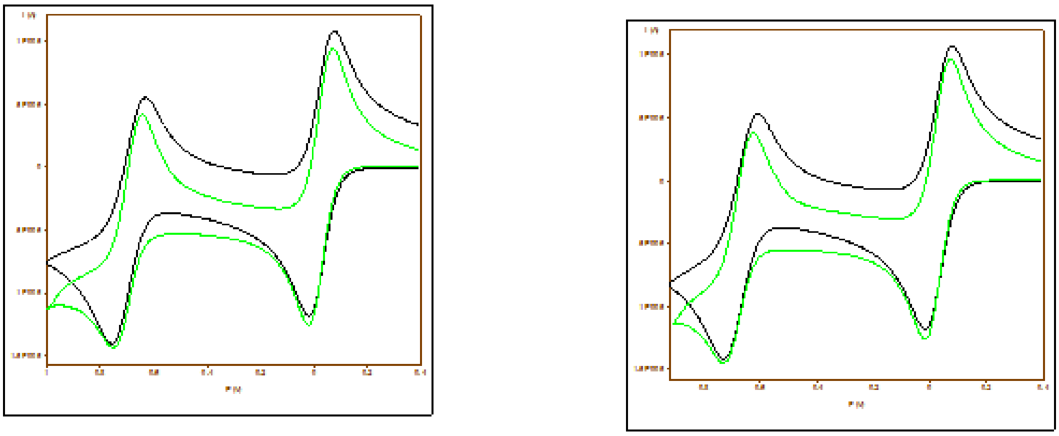
100 equiv. of **1**

Figure S7. Experimental (green) and simulated (black) cyclic voltamograms of TCQ (0.5 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in acetonitrile in the absence and in the presence of iodo-perfluorohexane (**1**). Scan rate 0.1 V/s.



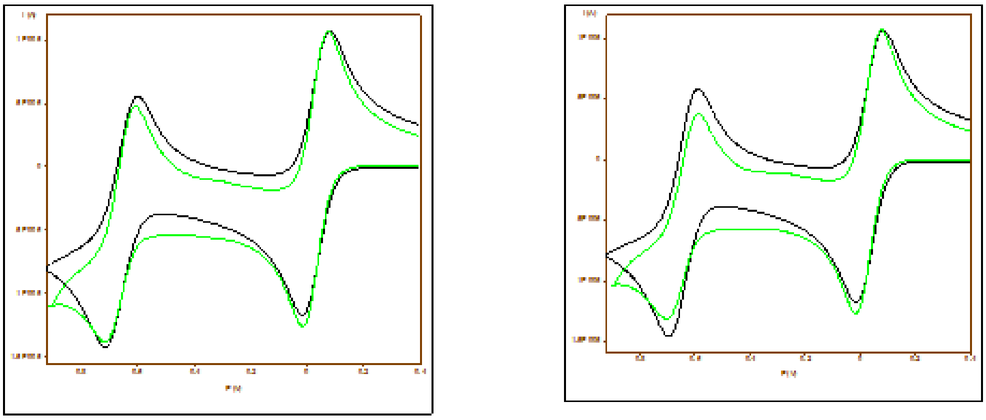
absence of **3**

1 equiv. of **3**



10 equiv. of **3**

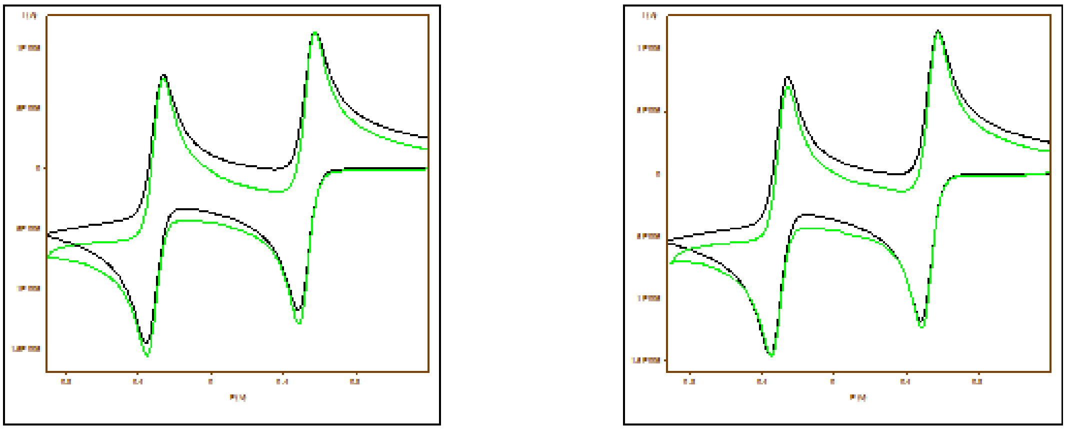
30 equiv. of **3**



50 equiv. of **3**

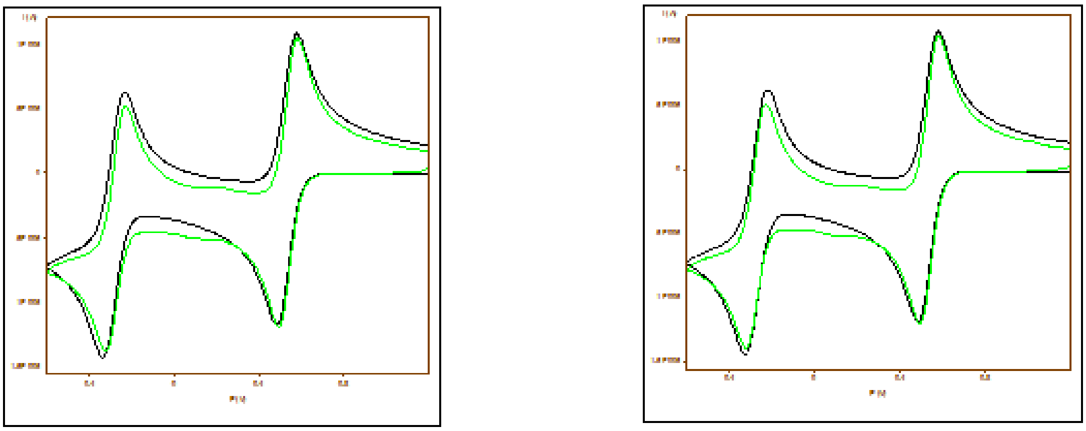
100 equiv. of **3**

Figure S8. Experimental (green) and simulated (black) cyclic voltamograms of TCQ (0.5 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in acetonitrile in the absence and in the presence of iodo-perfluorobenzene (**3**). Scan rate 0.1 V/s.



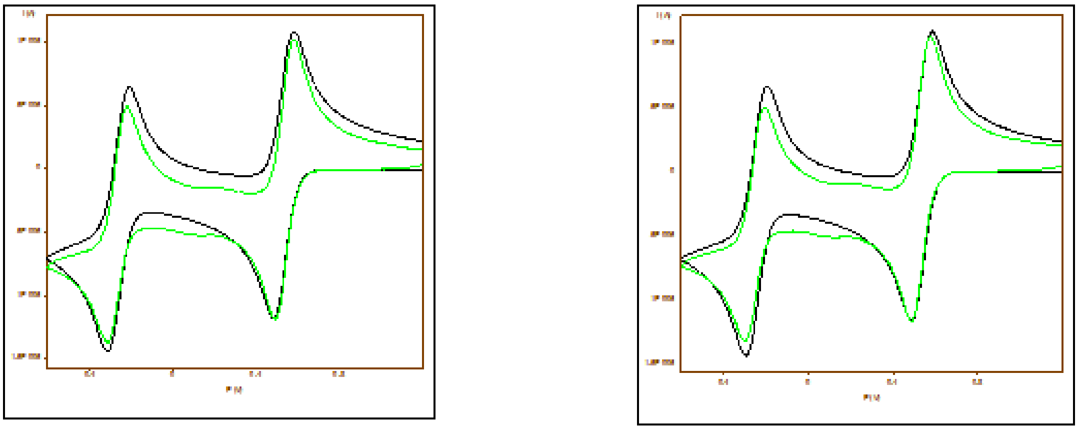
absence of **1**

1 equiv. of **1**



10 equiv. of **1**

20 equiv. of **1**



50 equiv. of **1**

100 equiv. of **1**

Figure S9. Experimental (green) and simulated (black) cyclic voltamograms of DDQ (0.5 mM) on a glassy carbon electrode in a solution of TBAPF$_6$ (0.1 M) in acetonitrile in the absence and in the presence of iodo-perfluorohexane (**1**). Scan rate 0.1 V/s.