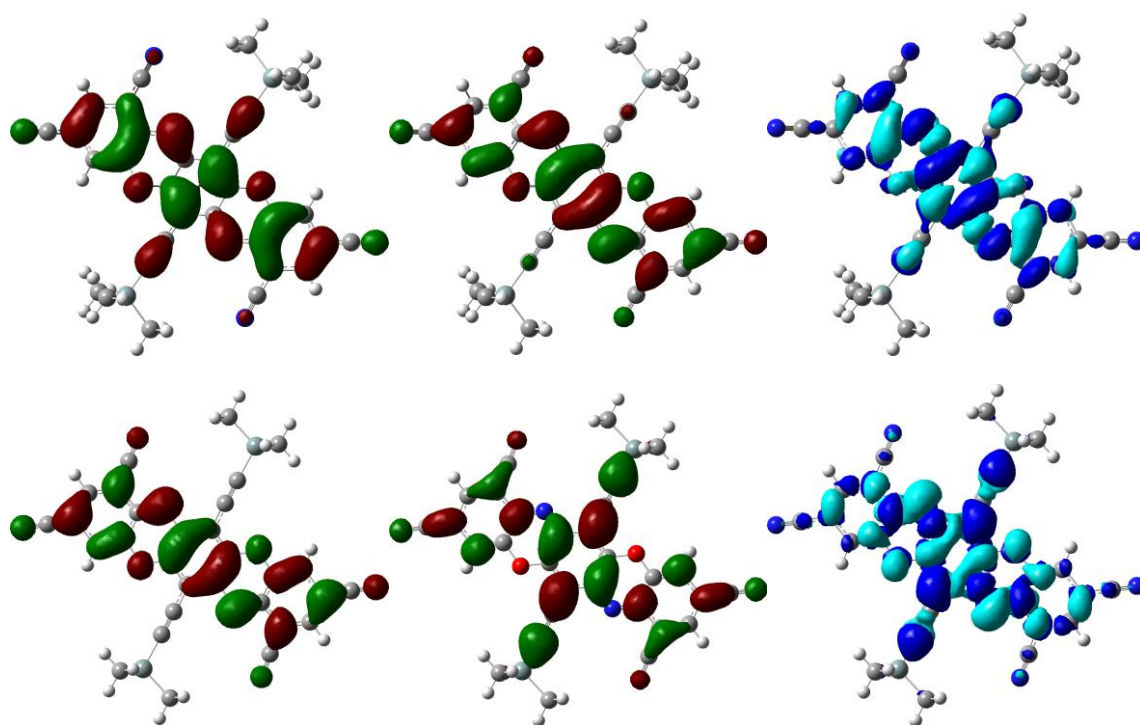


**Figure S1.** Absorption spectra of TiPS-TPDO-tetraCN (solid red line) and (TiPS-TPDO-tetraCN)<sup>2-</sup> (dashed blue line) calculated at the TDDFT/M06-2X/6-311+G(d) level. The theoretical absorption peaks were enlarged using Gaussian functions with a full width at half maximum (FWHM) of 0.5 eV.



**Figure S2.** HOMO (left), LUMO (middle) and electron density difference (right) between the lowest excited state and the ground state of TiPS-TPDO-tetraCN (top) and of the dianionic species (bottom). Blue (purple) lobes are associated with negative (positive) values.

## Digital simulations of cyclic voltammograms

They were performed in four successive steps noted from 1 to 4.

### 1- Study of the EE mechanism to determine the electrochemical rate constants

Digital simulations were performed to adjust the reduction peaks of both redox systems on the experimental voltammogram without addition of water. In the following simulations, we introduced the limit values:  $k_{s1} = 0.04 \text{ cm s}^{-1}$  and  $k_{s2} = 0.01 \text{ cm s}^{-1}$ .

Electrochemical reactions	Experimental data	Arbitrary chosen values	Fitted parameters
A + e = B	$E^{\circ}_1 = -0.113 \text{ V}$	$\alpha = 0.5$	$k_{s1} > 0.04 \text{ cm s}^{-1}$
B + e = C	$E^{\circ}_2 = -0.49 \text{ V}$	$\alpha = 0.5$	$k_{s2} \geq 0.01 \text{ cm s}^{-1}$
Species			
A	$C_A = 2 \cdot 10^{-4} \text{ M}$	$D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	
	$v = 0.1 \text{ V s}^{-1}$		

### 2- Digital simulations of the DISP mechanism alone

They were performed on the experimental voltammogram without addition of water

$K_2$  was calculated from the relation  $K_1\eta_2 = K_2\eta_3$  with  $\eta_i = \exp((F/RT)(E-E^{\circ}_i))$

It is not possible to fit perfectly the experimental voltammogram but this mechanism has the effect of decreasing the intensity of the second system.

Electrochemical reactions	Experimental data	Arbitrary chosen values	Fitted parameters	Parameters deduced from the other constants
A + e = B	Same parameters as in 1-			
B + e = C				
D + e = E		$\alpha = 0.5$	$E^{\circ}_3$	
Chemical reactions				
B = D			$K_1$	
C = E				$K_2$
B + D = A + E			$K_{DISP}$	

### 3- Digital simulations of the mechanism involving H<sub>2</sub>O molecules

They were performed on the experimental voltammograms with addition of 1 and 2 M H<sub>2</sub>O. It is not possible to fit perfectly the experimental voltammograms. This mechanism has the effect of decreasing the reversibility of both systems and therefore decreasing too much the anodic peaks. It also induced diminishing the intensity of the cathodic peak of the second system.

Electrochemical reactions	Experimental data	Arbitrary chosen values	Fitted parameters	Parameters deduced from the other constants
A + e = B	Same parameters as in 1-			
B + e = C				
F + e = G	$E^{\circ}_4$	$\alpha = 0.5$		
Chemical reactions				
B = F			$K_4$	
C = G				$K_5$
G = H			$K_6$	
Species				
H <sub>2</sub> O	$C_{H_2O} = 1 \text{ M}$ $C_{H_2O} = 2 \text{ M}$	$D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$		

#### 4- Digital simulations of the complete mechanism

Neither the DISP mechanism nor the mechanism involving reactions with water can alone reflect the experimental results. Therefore, both must be considered to fit properly the experimental voltammograms with addition of 1 and 2 M H<sub>2</sub>O.

In order to better understand the influence of each chemical reaction on the shape of the voltammogram, we performed several series of simulations by varying one constant at a time and the best results were kept in the final simulation.

Electro-chemical reactions	Experimental data	Arbitrary chosen values	Parameters obtained from the other simulations	Parameters deduced from the other constants	Fitted parameters
A + e = B	$E^{\circ}_1 = -0.113 \text{ V}$	$\alpha = 0.5$	$k_{s1} = 0.04 \text{ cm s}^{-1}$		
B + e = C	$E^{\circ}_2 = -0.49 \text{ V}$	$\alpha = 0.5$	$k_{s2} = 0.01 \text{ cm s}^{-1}$		
D + e = E		$\alpha = 0.5$	$E^{\circ}_3 = -0.105 \text{ V}$ $k_{s3} = 0.02 \text{ cm s}^{-1}$		
F + e = G		$\alpha = 0.5$	$k_{s4} = 0.02 \text{ cm s}^{-1}$	$E^{\circ}_4$	
Chemical reactions					
B = D			$K_1, k_{f1}$		
C = E				$K_2, k_{f2}$	
B + D = A + E				$K_{DISP}, k_{fDISP}$	
A + H <sub>2</sub> O = I			$K_3, k_{f3}$		
B + H <sub>2</sub> O = F			$K_4$		$k_{f4}$
C + H <sub>2</sub> O = G				$K_5$	$k_{f5}$
G = H			$K_6$		$k_{f6}$
Species					
A	$C_A = 2 \cdot 10^{-4} \text{ M}$	$D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$			
H <sub>2</sub> O	$C_{H_2O} = 1 \text{ M}$ $C_{H_2O} = 2 \text{ M}$	$D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$			
	$v = 0.1 \text{ V s}^{-1}$				
	$Cdl = 6 \mu\text{F}$				
	$R = 1000 \Omega$				

