

## Electronic Supplementary Information

### Preparation and Optoelectronic Behaviours of Novel Electrochromic Devices Based on Triphenylamine-containing Ambipolar Materials

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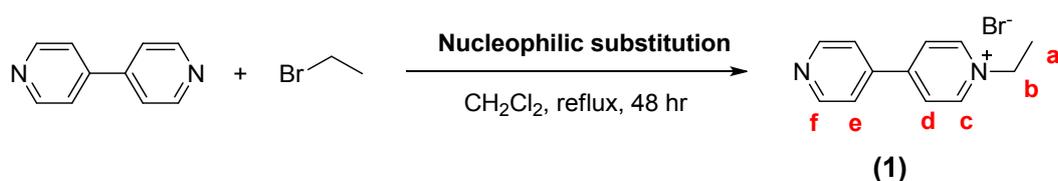
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## Experimental Section

### Measurements:

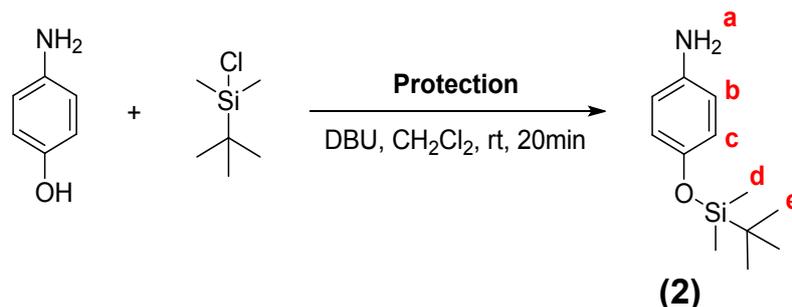
$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker DPX-400 MHz FT-NMR, and peak multiplicity was reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses were run in a Heraeus VarioEL-III CHNS elemental analyzer. Electrochemistry was performed with a CH Instruments 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the right and with increasing anodic currents pointing upwards. Cyclic voltammetry (CV) was conducted with the use of an optically transparent thin layer electrochemical (OTTLE) cell. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. Spectroelectrochemical experiments were carried out in a cell built from a 1 cm commercial UV-vis cuvette using Hewlett-Packard 8453 UV-vis diode array spectrophotometer. The CIELAB data were collected from JASCO V-650. The platinum net was used as the working electrode, while wire as the counter electrode, and an Ag/AgCl cell as the reference electrode. CE ( $\eta$ ) determines the amount of optical density change ( $\Delta\text{OD}$ ) at a specific absorption wavelength induced as a function of the ejected/injected charge ( $Q$ ; also termed as electroactivity) by the in situ experiments. CE is given by the equation:  $\eta = \Delta\text{OD}/Q = \log[T_b/T_c]/Q$ , where  $\eta$  ( $\text{cm}^2/\text{C}$ ) is the coloration efficiency at a given wavelength,  $Q$  means the injected charge, and  $T_b$  and  $T_c$  are the transmittance values for bleached and colored state, respectively.

### 1-Ethyl-[4,4'-bipyridin]-1-ium bromide (1)



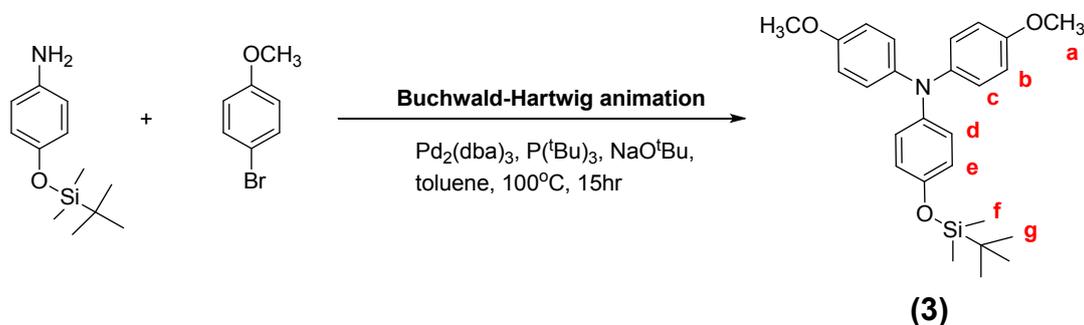
10.0 g (64.0 mmol) of 4,4'-bipyridyl and 200 mL of dichloromethane were added to a 500 mL three-necked round-bottom flask equipped with a stirring bar and a reflux condenser. Then, 50.0 mL (80.0 mmol) of ethyl bromide was dropped in the flask. The mixture was heated with stirring at reflux state for 48 hours when a white precipitate formed. The precipitated white solids were filtered out and dried to give 14.4 g (85 % in yield) of the product. Mp = 188-190 °C.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 1.58 (t, 3H,  $H_a$ ), 4.68-4.63 (qtet, 2H,  $H_b$ ), 8.04 (d, 2H,  $H_c$ ), 8.63 (d, 2H,  $H_e$ ), 8.87 (d, 2H,  $H_d$ ), 9.26 (d, 2H,  $H_f$ ). These results agreed well with previous literature<sup>S1</sup>.

#### 4-(*tert*-Butyldimethylsilyloxy)phenylamine (2)



To a solution of 4-aminophenol (5.46 g, 50 mmol) and *tert*-butyl(chloro)dimethylsilane (55 mmol) in anhydrous dichloromethane (150 mL) was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (80 mmol). The target mixture was stirred at room temperature under a nitrogen atmosphere for 20 minutes, as monitored by thin-layer chromatography (TLC). The solution was washed successively with water (100 mL), 0.1 M HCl (100 mL), and saturated aqueous NaHCO<sub>3</sub> (100 mL). The organic layer was dried over anhydrous MgSO<sub>4</sub> to acquire the product as brown oil (72% in yield). <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm): 0.10 (s, 6H, H<sub>d</sub>), 0.92 (s, 9H, H<sub>e</sub>), 4.60 (s, 2H, H<sub>a</sub>), 6.48 (d, 4H, H<sub>b+c</sub>). These results agreed well with literature<sup>S2</sup>.

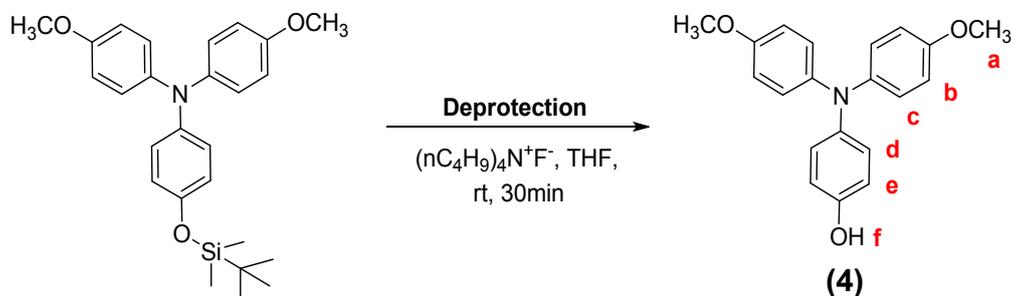
#### 4-{{*tert*-Butyl(dimethyl)silyl}oxy}-*N,N*-bis(4-methoxyphenyl)aniline (3)



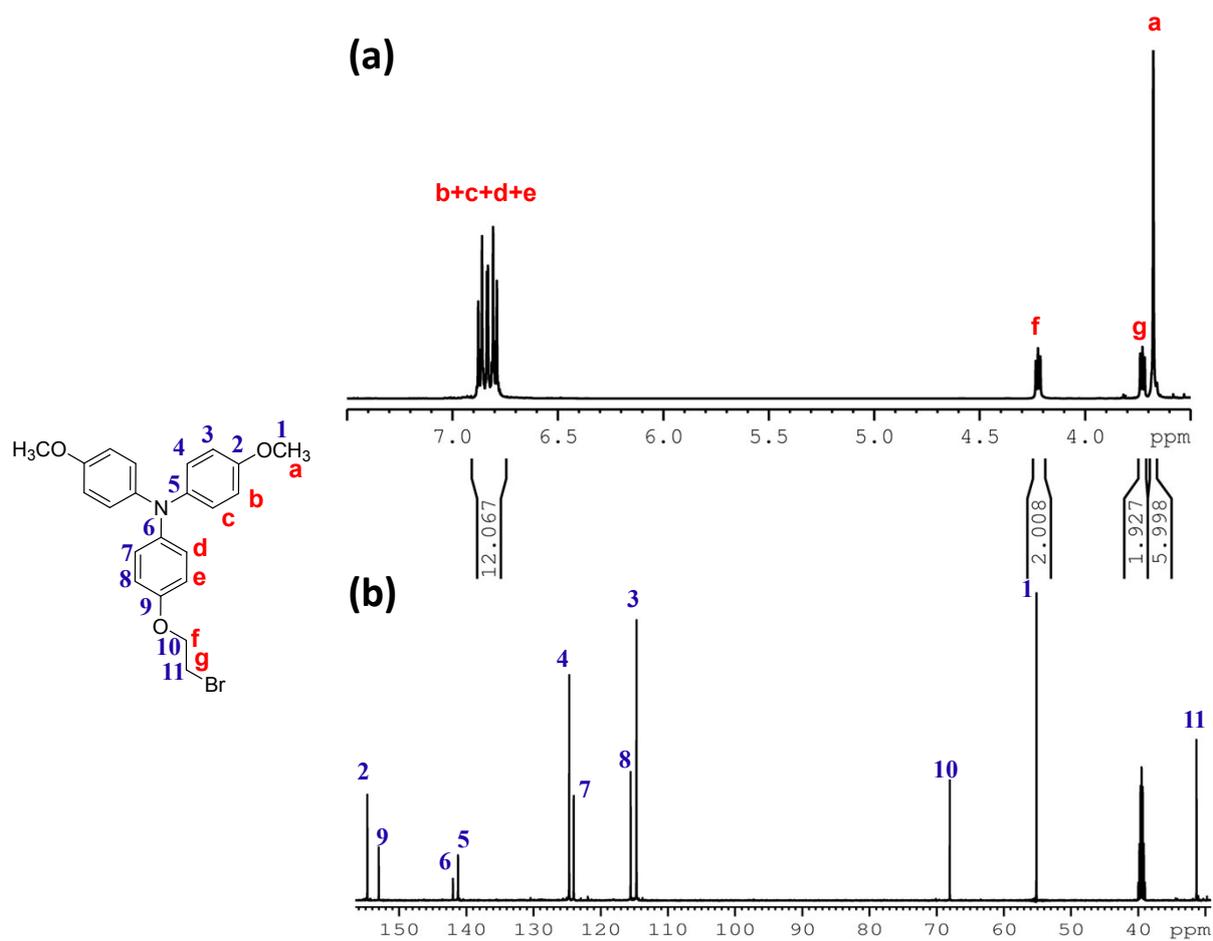
Tris(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>; 93.5 mg, 0.102 mmol), and tri-*tert*-butylphosphine (P(*t*Bu)<sub>3</sub>; 114 mg, 0.610 mmol) were dissolved in dry toluene (80 mL) under nitrogen atmosphere. After stirring for 10 minutes to provide chemical catalysis at room temperature, 4-bromoanisole (5.70 g, 30.5 mmol) was added to flask and stirred for next 10 minutes. 4-(*tert*-Butyldimethylsilyloxy)phenylamine (2.27 g, 10.2 mmol), and sodium *tert*-butoxide (NaO*t*Bu; 2.34 g, 24.4 mmol) were successively put in the reactor. The solution was stirred at 100 °C for 15 h. After cooling to room tem, the reaction mixture was diluted with ethyl acetate (100 mL) and washed with brine (100 mL x 2). The organic layer was dried over MgSO<sub>4</sub>. Evaporation and column chromatography (SiO<sub>2</sub>, hexane/ethyl acetate = 4:1) afforded the desired product (2.1 g, 50 %) as a yellow solid. mp: 69-70 °C (by Melting Point System at a

scan rate of 5 °C/ min). (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 0.17 (s, 6H,  $H_f$ ), 0.94 (s, 9H,  $H_g$ ), 3.71 (s, 6H,  $H_a$ ), 6.75 (d, 4H,  $H_{e+d}$ ), 6.86 (d, 8H,  $H_{b+c}$ ). These results agreed well with literature<sup>S2</sup>.

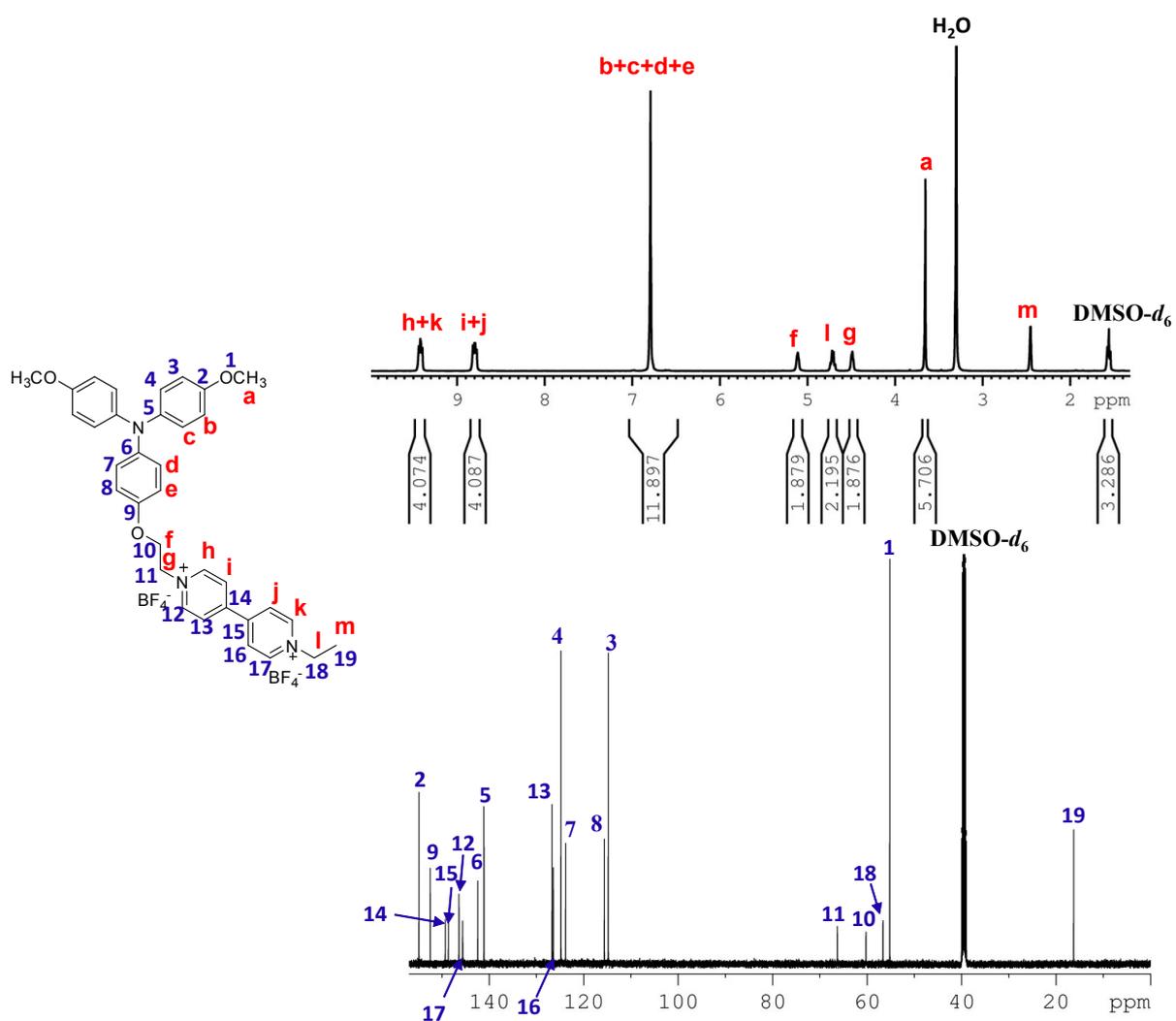
#### 4-[Bis(4-methoxyphenyl)amino]phenol (4)



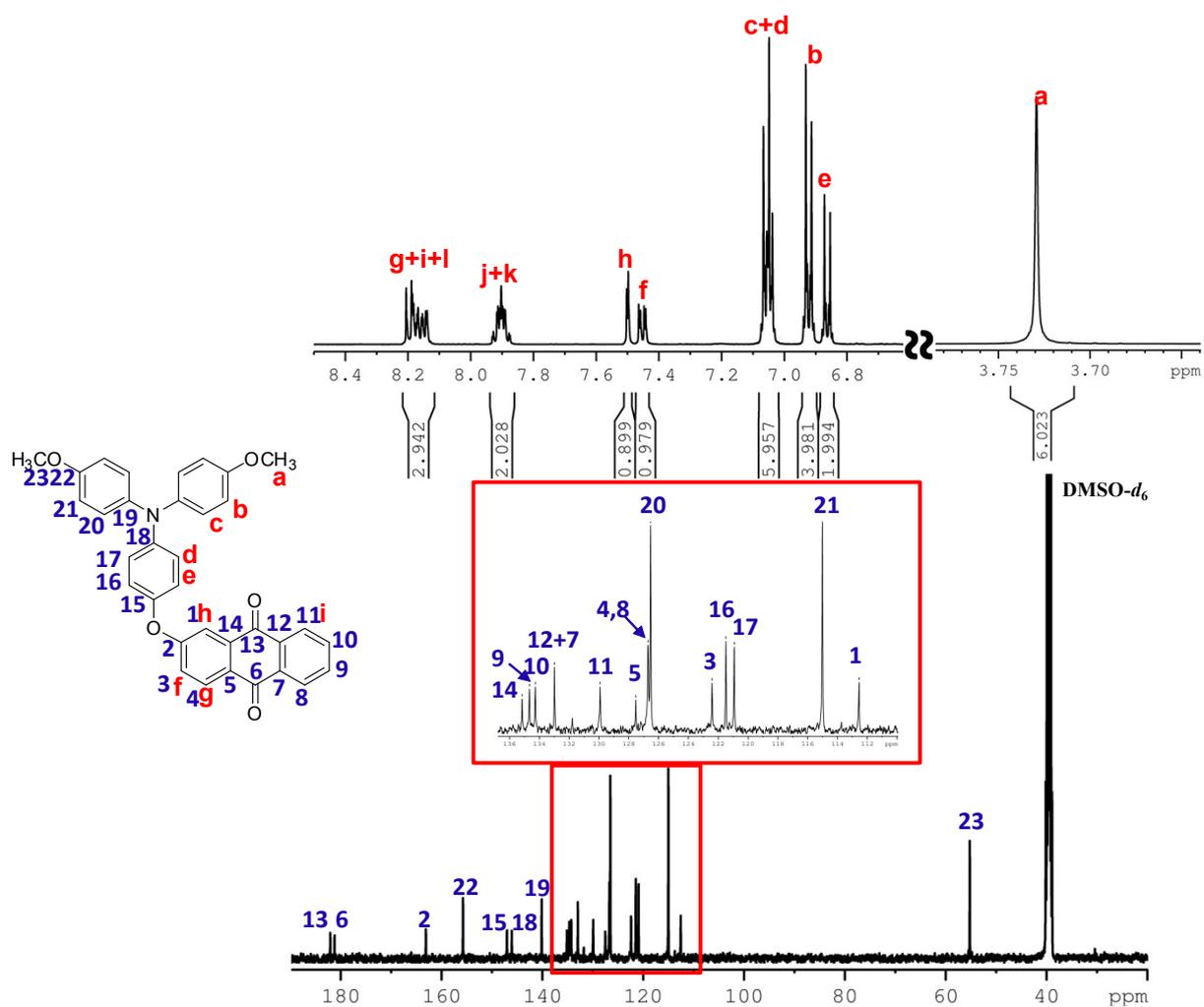
To a solution of 4-[[*tert*-butyl(dimethyl)silyl]oxy]-*N,N*-bis(4-methoxyphenyl)aniline (3.01 g, 6.90 mmol) in THF (60 mL), tetrabutylammonium fluoride (1 M in THF, 7 mL) was added under nitrogen atmosphere. The mixture was stirred at 20 °C for 20 min monitored by TLC and then washed with water and ethyl acetate. After drying with rotary evaporator, it obtained the target product (2.0 g, 90 % in yield) as brown oil. (400 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 3.69 (s, 6H,  $H_a$ ), 6.68 (d, 2H,  $H_e$ ), 6.80 (m, 10H,  $H_{b+c+d}$ ), 9.19 (s, 1H,  $H_f$ ). These results agreed well with literature<sup>S2</sup>.



**Fig. S1** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of TPA-OBr (5) in  $\text{DMSO-}d_6$ .



**Fig. S2** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of TPA-Vio (6) in DMSO-*d*<sub>6</sub>.



**Fig. S3** (a)  $^1\text{H}$  NMR and (b)  $^{13}\text{C}$  NMR spectra of TPA-OAQ (7) in  $\text{DMSO-}d_6$ .

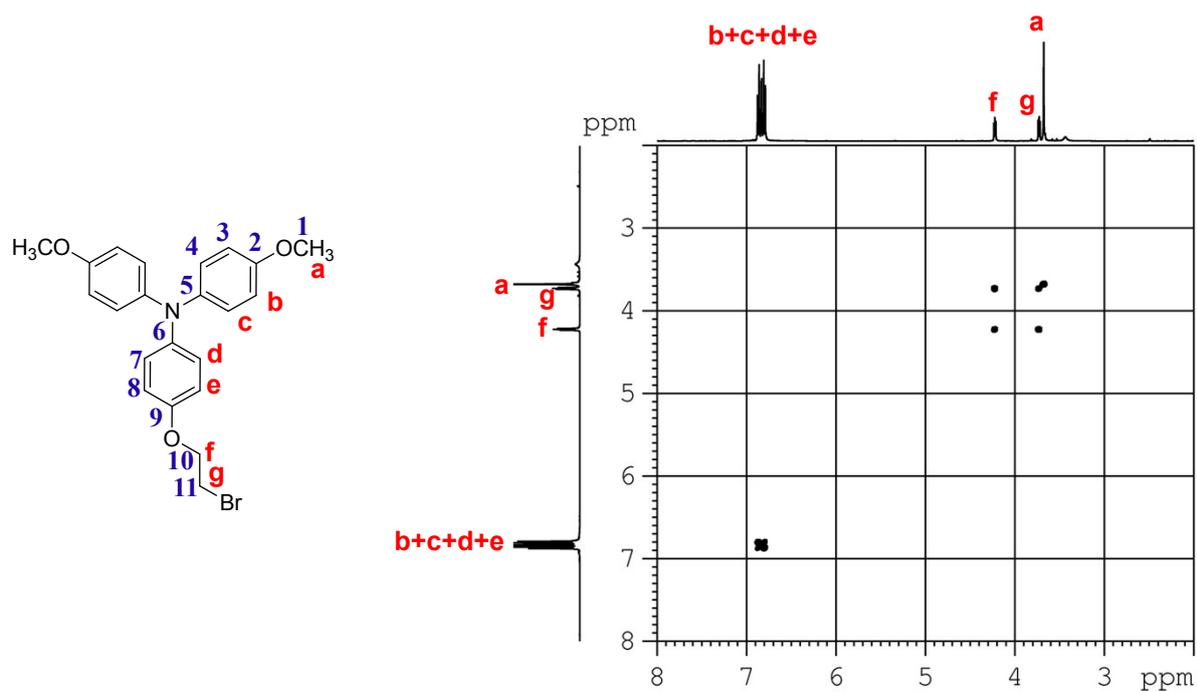


Fig. S4 2D H-H COSY NMR spectra of TPA-OBr (5) in DMSO-*d*<sub>6</sub>.

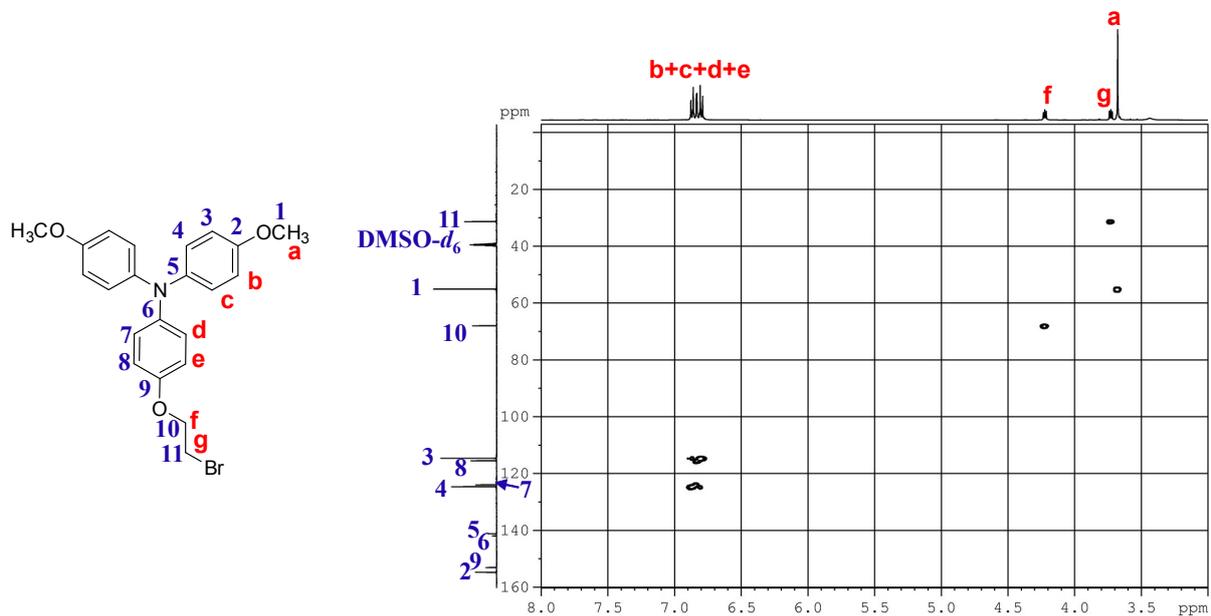


Fig. S5 2D C-H HMQC NMR spectra of TPA-OBr (5) in DMSO-*d*<sub>6</sub>.

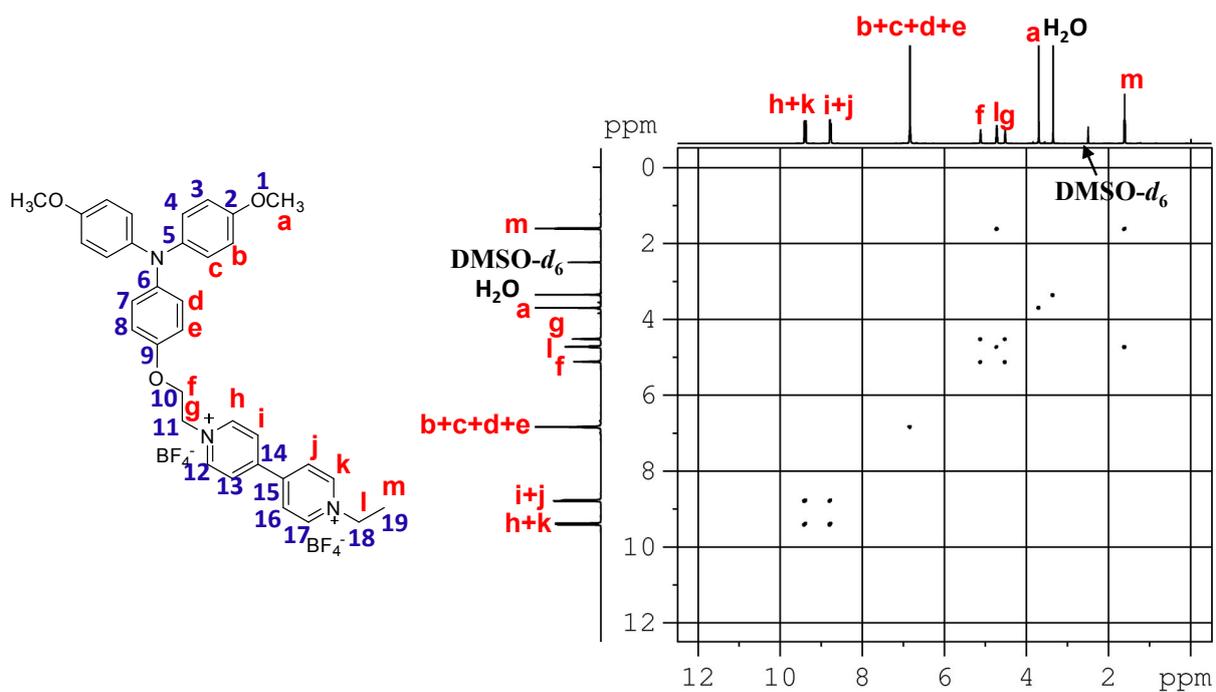


Fig. S6 2D H-H COSY NMR spectra of TPA-Vio (6) in DMSO-*d*<sub>6</sub>.

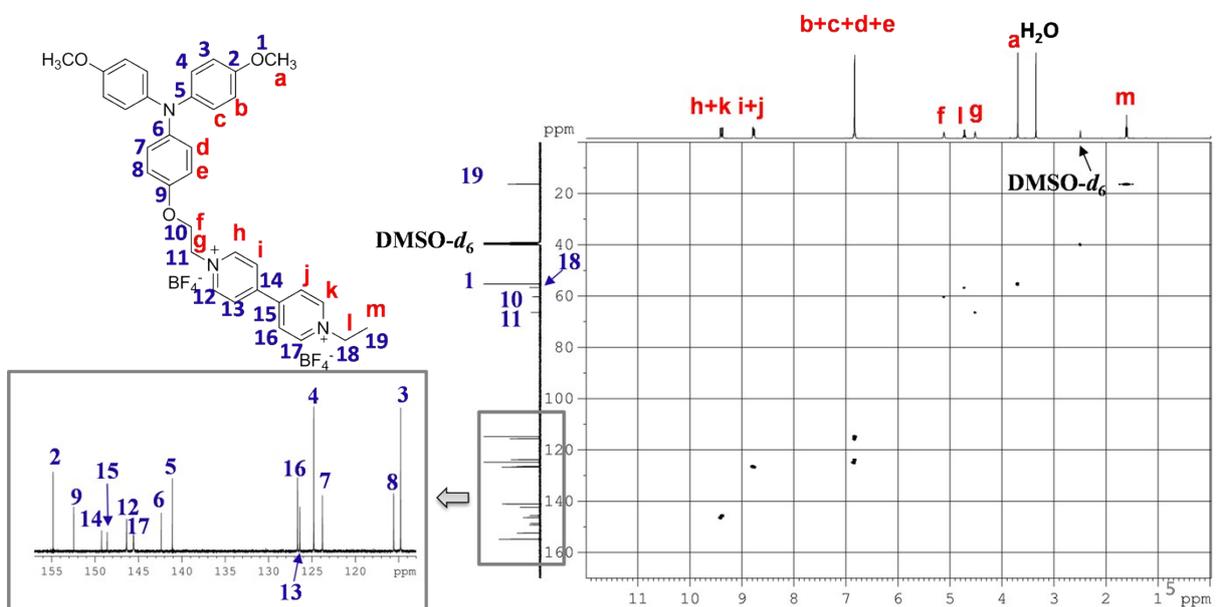
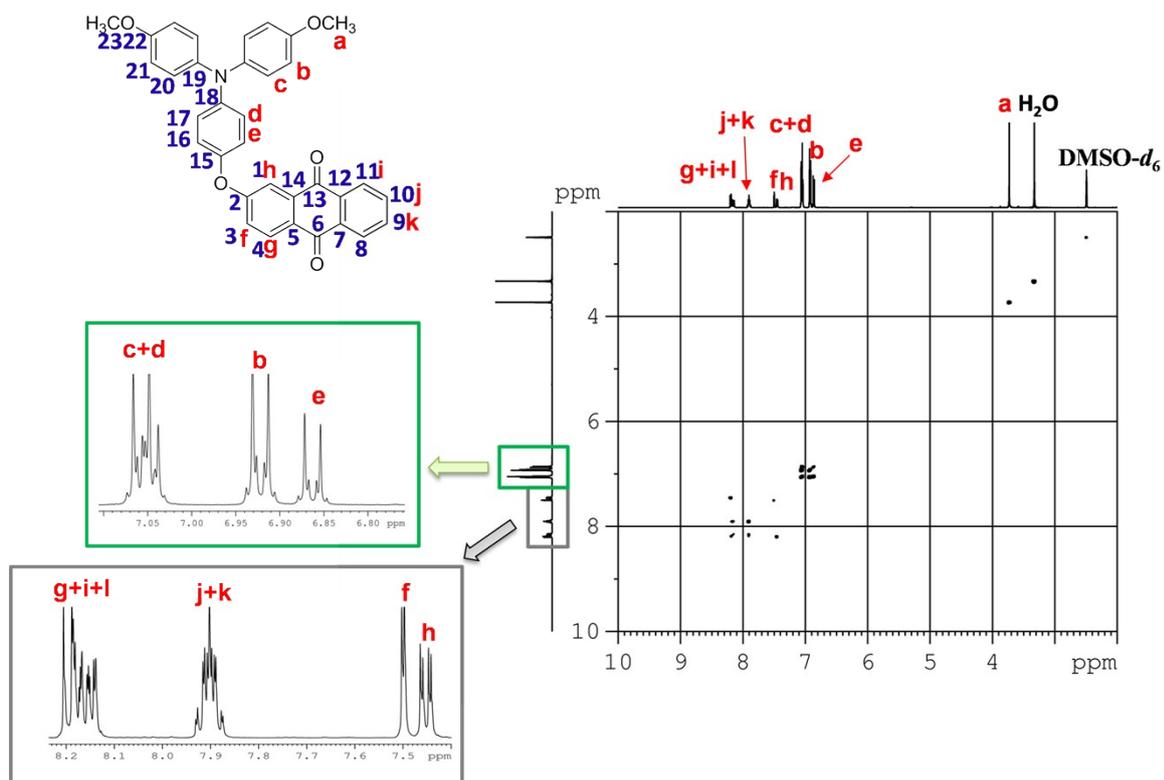
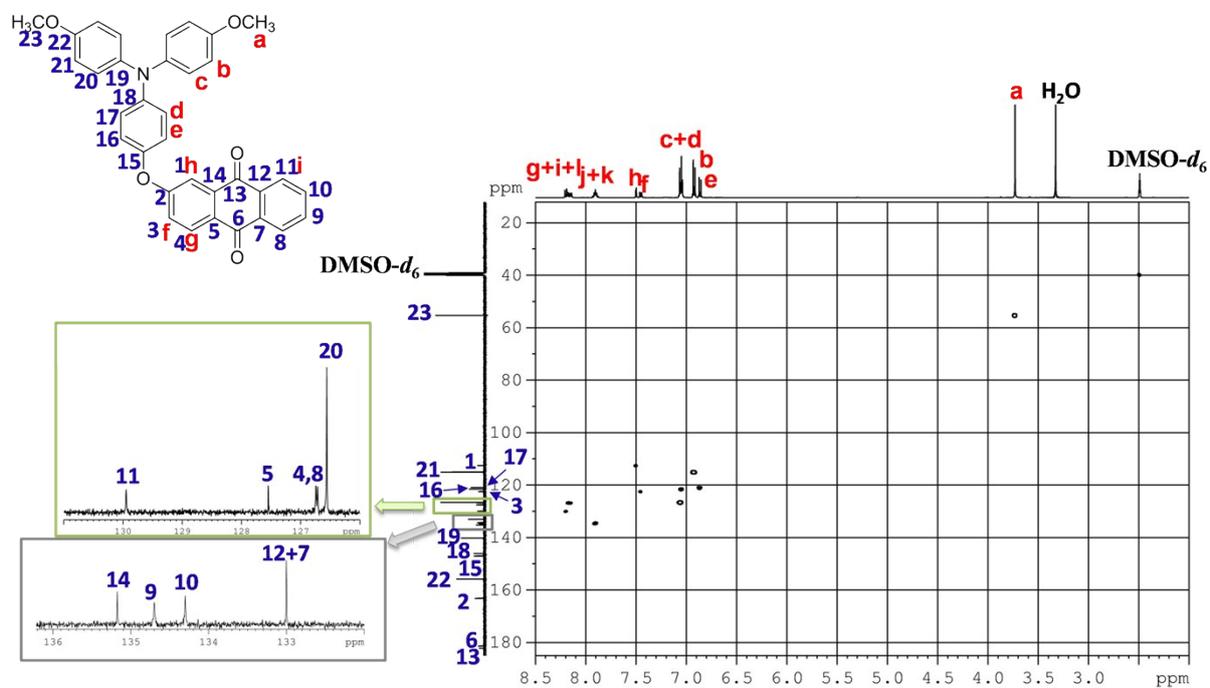


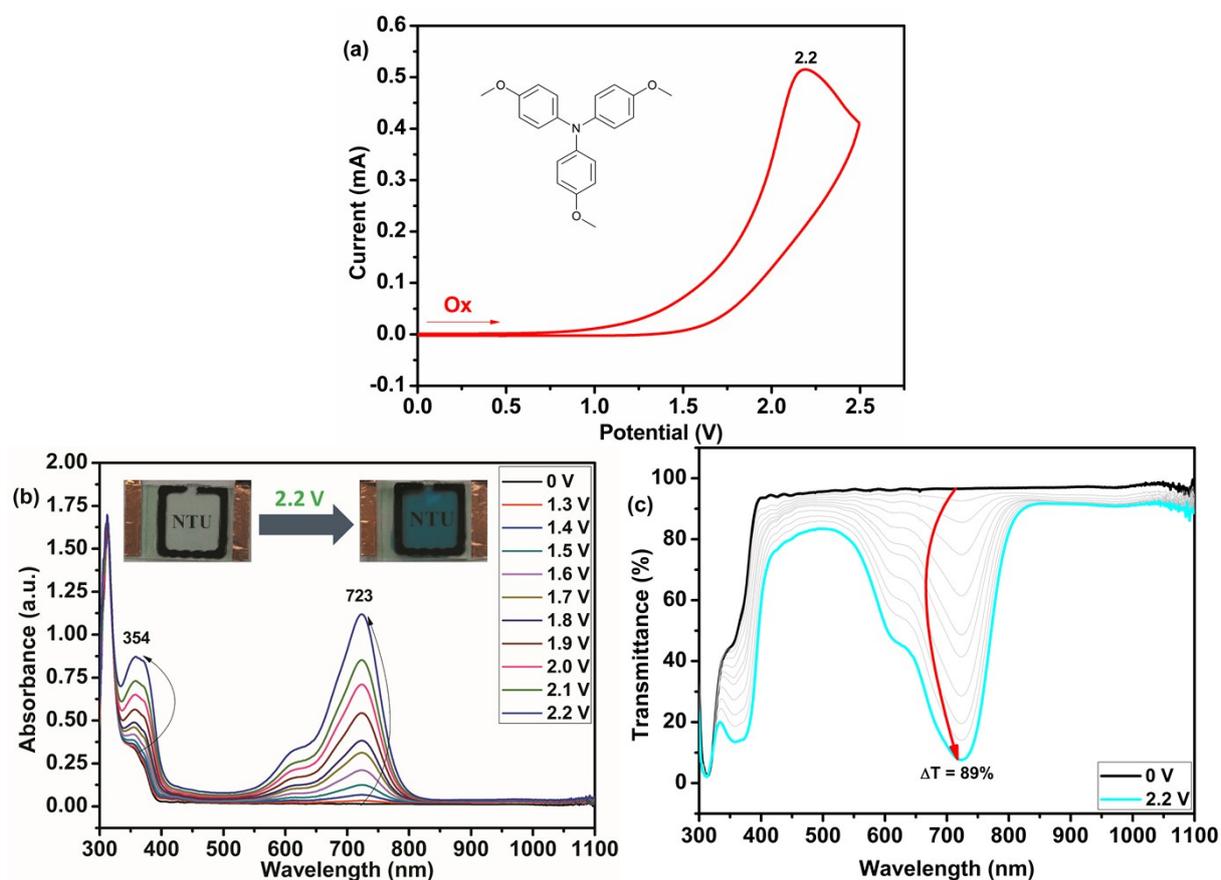
Fig. S7 2D C-H HMQC NMR spectra of TPA-Vio (6) in DMSO-*d*<sub>6</sub>.



**Fig. S8** 2D H-H COSY NMR spectra of TPA-OAQ in DMSO- $d_6$ .



**Fig. S9** 2D C-H HMQC NMR spectra of TPA-OAQ (7) in DMSO- $d_6$ .



**Fig. S10** (a) CV diagram at the scan rate of 50 mV/s, (b) absorbance spectra, photographs, and (c) transmittance spectra at the applied potential from 0 to 2.2 V for the ECD derived from 0.015 M of **TPA-3OMe** in the PC solution containing 0.1 M of TBABF<sub>4</sub>.

**Table S1** Optical and electrochemical data collected for coloration efficiency measurements of device with **TPA-3OMe**.

cycling times <sup>a</sup>	$\Delta OD^b$	Q (mC/cm <sup>2</sup> ) <sup>c</sup>	$\eta$ (cm <sup>2</sup> /C) <sup>d</sup>	Decay (%) <sup>e</sup>
	724 nm		724 nm	724 nm
1	1.878	10.993	171	0
20	0.832	6.064	137	19.88

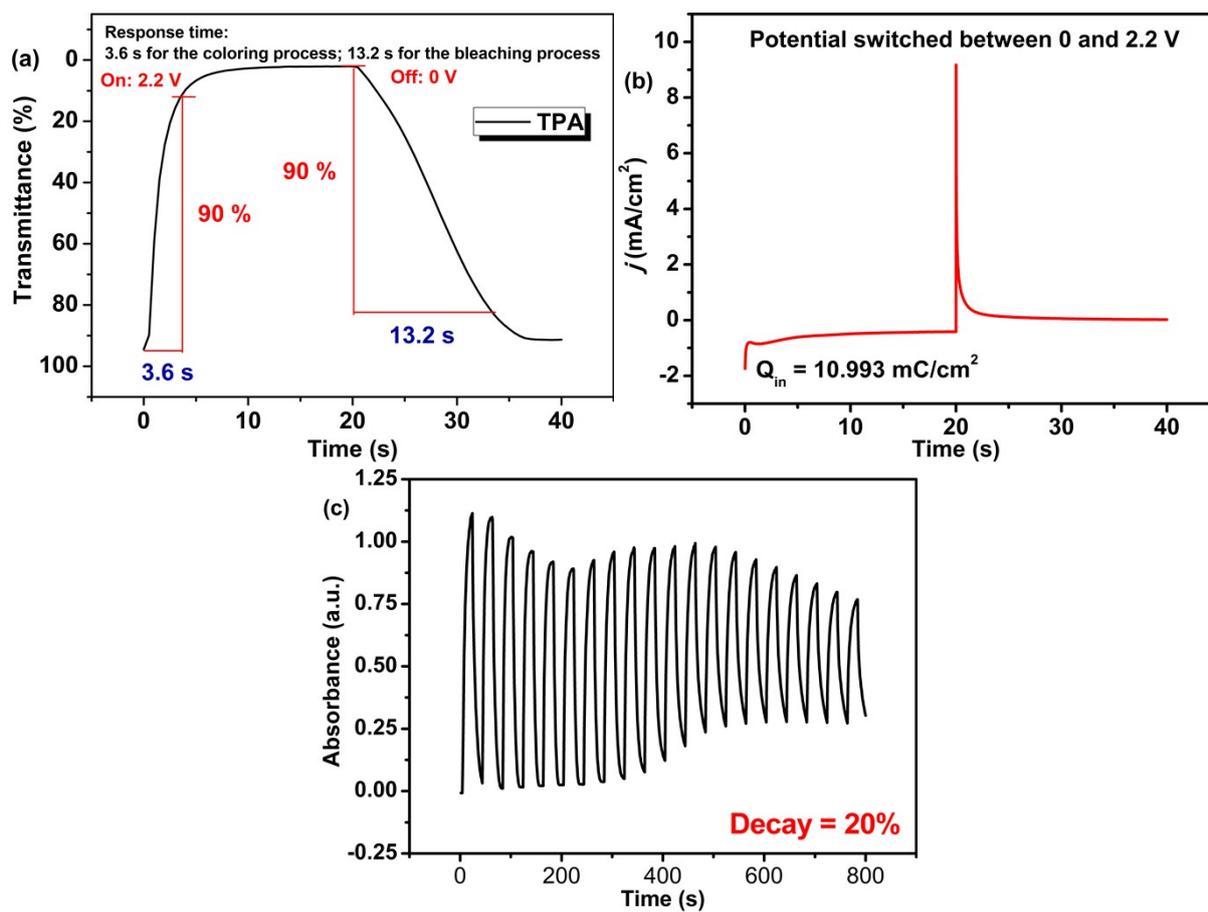
<sup>a</sup> Switching between 0 and 2.2 V for EC device with **TPA-3MeO**.

<sup>b</sup> Absorbance change at the specific wavelength.

<sup>c</sup> Ejected charge, determined from the in situ experiments.

<sup>d</sup> Coloration efficiency;  $\eta = \Delta OD / Q$

<sup>e</sup> Decay of CE after various switching scans



**Fig. S11** (a) Transmittance change at 724 nm, (b) chronoamperometry curve, and (c) absorbance changes at 724 nm of the ECD based on **TPA-3OMe** between 0 and 2.2 V for 20 cycles.

**Table S2** Optical and electrochemical data collected for coloration efficiency measurements of device with **TPA-Vio**.

cycling times <sup>a</sup>	$\Delta OD^b$		Q (mC/cm <sup>2</sup> ) <sup>c</sup>	$\eta$ (cm <sup>2</sup> /C) <sup>d</sup>		Decay (%) <sup>e</sup>	
	606 nm	724 nm		606 nm	724 nm	606 nm	724 nm
1	1.563	2.485	14.012	112	177	0	0
100	1.546	2.462	13.946	111	177	0.89	0
200	1.542	2.416	13.886	111	174	0.89	1.69
300	1.499	2.364	13.791	109	171	2.68	3.39
400	1.491	2.369	13.623	109	174	2.68	1.69
500	1.456	2.346	13.547	108	173	3.57	2.26
600	1.456	2.342	13.470	108	174	3.57	1.69
700	1.411	2.341	13.431	105	174	6.25	1.69
800	1.404	2.322	13.364	105	174	6.25	1.69
900	1.387	2.276	13.250	105	172	6.25	2.82
1000	1.368	2.199	13.196	104	167	7.14	5.65

<sup>a</sup> Switching between 0 and 1.2 V for EC device with **TPA-Vio (6)**.

<sup>b</sup> Absorbance change at the specific wavelength.

<sup>c</sup> Ejected charge, determined from the in situ experiments.

<sup>d</sup> Coloration efficiency,  $\eta = \Delta OD / Q$ .

<sup>e</sup> Decay of CE after various switching scans.

**Table S3** Optical and electrochemical data collected for coloration efficiency measurements of device with **TPA-OAQ**.

cycling times <sup>a</sup>	$\Delta OD^b$		Q (mC/cm <sup>2</sup> ) <sup>c</sup>	$\eta$ (cm <sup>2</sup> /C) <sup>d</sup>		Decay (%) <sup>e</sup>	
	535 nm	734 nm		535 nm	734 nm	535nm`	734 nm
1	1.032	2.288	14.134	73	162	0	0
100	0.988	2.223	14.185	70	157	4.11	3.09
200	0.979	2.184	14.090	69	155	5.48	4.32
300	0.974	2.186	14.083	69	155	5.48	4.32
400	0.957	2.202	13.710	70	160	4.11	1.23
500	0.925	2.109	12.868	72	164	1.37	-1.23
600	0.859	1.991	12.695	68	157	6.85	3.09
700	0.834	1.937	12.586	66	154	9.59	4.94
800	0.819	1.917	12.293	67	156	8.22	3.70
900	0.798	1.880	12.340	65	152	10.96	6.17
1000	0.789	1.848	12.030	66	154	9.59	4.94

<sup>a</sup> Switching between 0 and 1.8 V for EC device with **TPA-OAQ (7)**.

<sup>b</sup> Absorbance change at the specific wavelength.

<sup>c</sup> Ejected charge, determined from the in situ experiments.

<sup>d</sup> Coloration efficiency,  $\eta = \Delta OD / Q$ .

<sup>e</sup> Decay of CE after various switching scans.

## Notes and References

S1. J. H. Mondal, S. Ahmed and D. Das, *Langmuir*, 2014, **30**, 8290-8299.

S2. N. M. O'Boyle, J. K. Pollock, M. Carr, A. J. S. Knox, S. M. Nathwani, S. Wang, L. Caboni, D. M. Zisterer and M. J. Meegan, *J. Med. Chem.*, 2014, **57**, 9370-9382.