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Achieving Large Contrast, Low Driving Voltage, and High Stability Electrochromic Device with a Viologen Chromophore

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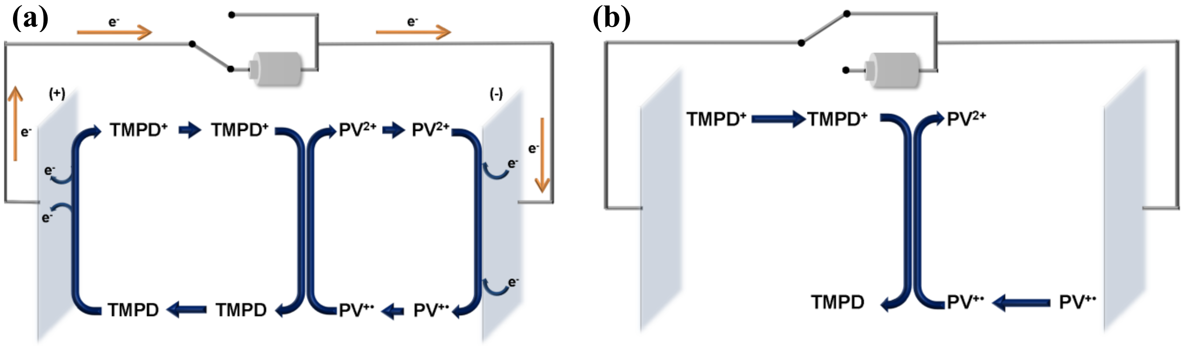

Scheme S1. Working principle of ECD containing PV and TMPD under (a) biasd potenital and (b) short-circuit condition.

Table S1. Electrochromic performance of ECD containing various concentration ratios of [TMPD]/[VRS].

[TMPD]/[VRS]	λ (nm)	T_b (%)	T_c (%)	τ_b (s)	τ_c (s)	ΔT (%)
0.5	580	76.3	34.5	1.9	2.7	41.8
0.5	620	75.8	30.2	1.9	2.6	45.6
1.0	580	75.1	31.9	2.7	2.7	43.2
1.0	620	75.1	28.1	2.7	2.7	47.6
2.0	580	75.7	18.3	2.7	2.7	57.4
2.0	620	75.8	15.9	2.7	2.7	59.9
4.0	580	75.3	15.1	2.7	2.7	60.2
4.0	620	75.2	12.6	2.7	2.7	62.6
6.0			Very unstable			

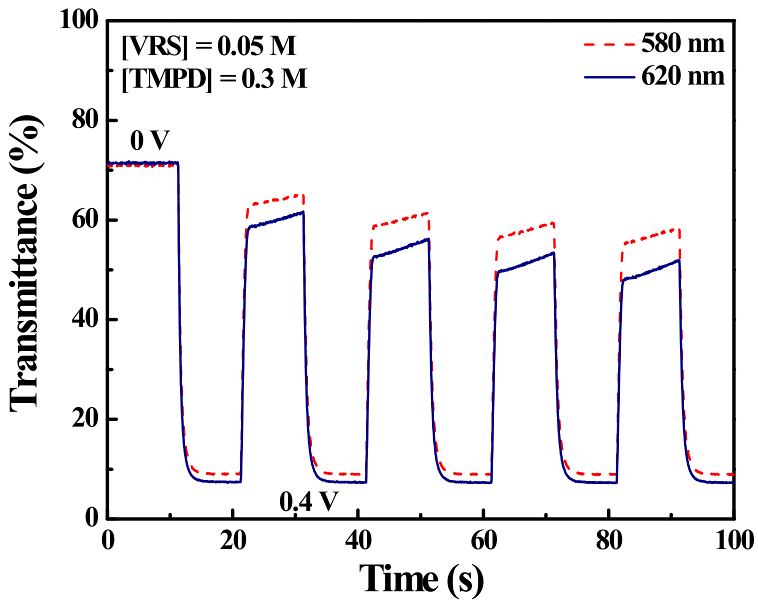

Figure S1. The dynamic transmittance (T) curves of an ECD with [TMPD] = 0.3 M and [VRS] = 0.05 M. Both coloring and bleaching intervals are set at 10 s.

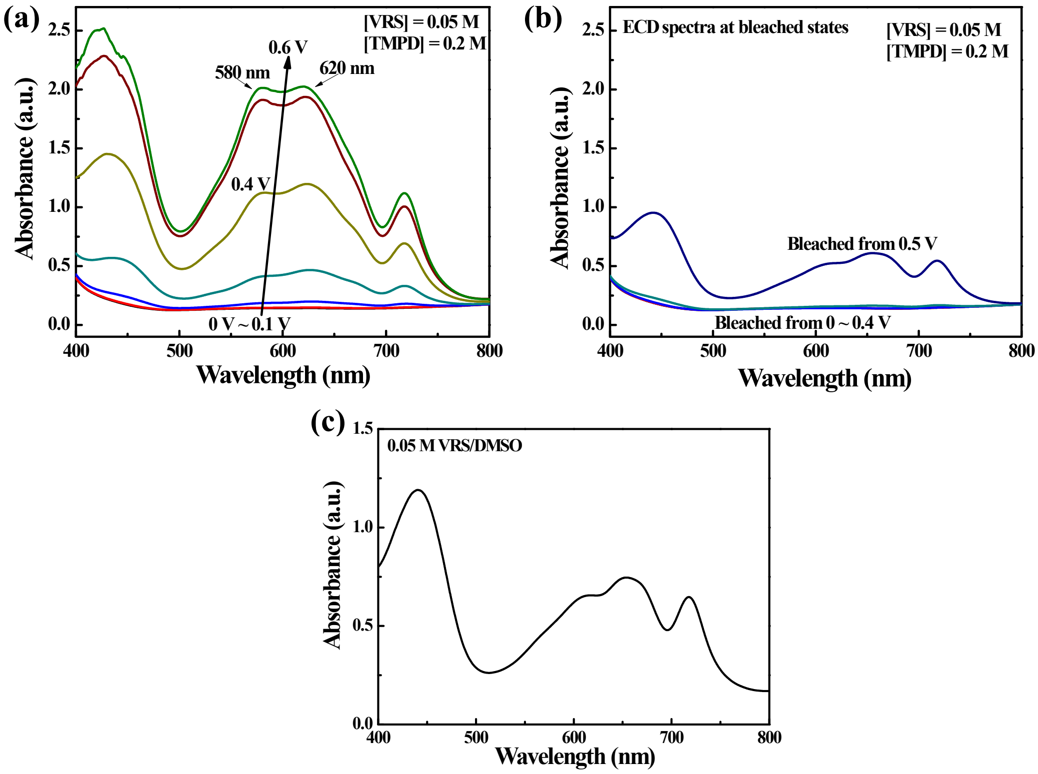

Figure S2. (a) The variation in absorbance in response to the potential bias (0 to 0.6 V) for the proposed ECD with [VRS] = 0.05 M and [TMPD] = 0.2 M. (b) The absorbance of the ECD in the bleached state after applying coloring potential of 0.1 ~ 0.4 V and 0.5 V. (c) UV-Vis absorption spectrum of VRS at the colored state.

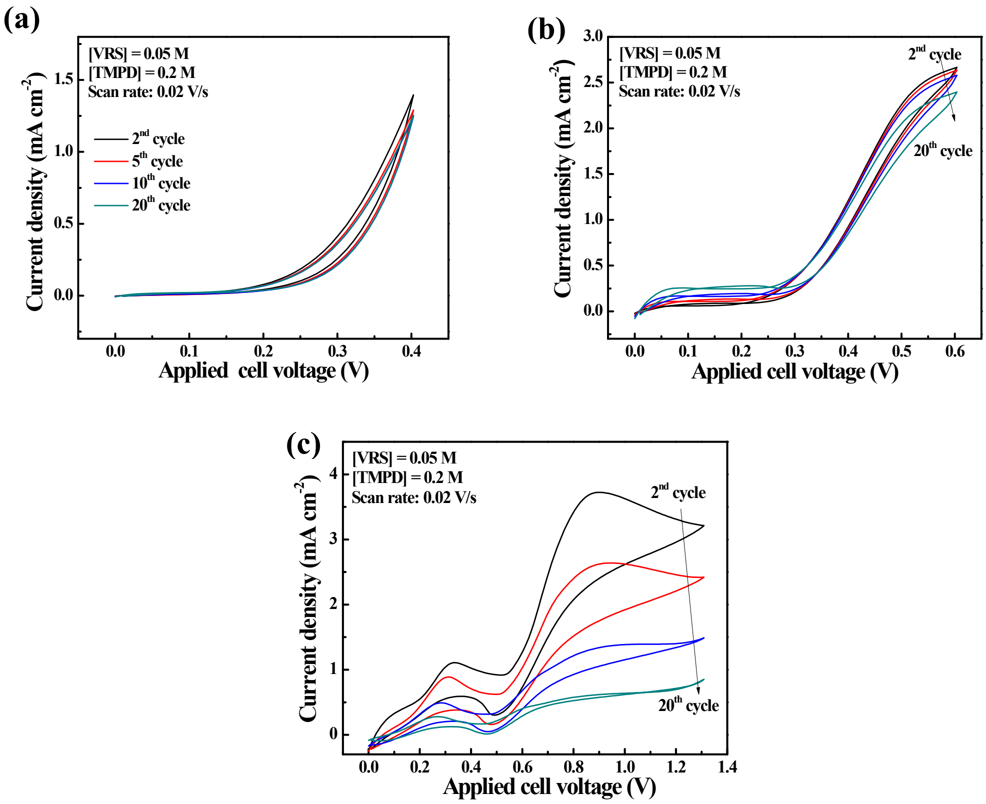

Figure S3. Cyclic voltammograms of an ECD scanned for the first 20 cycles in the potential ranges of (a) 0 ~ 0.4 V, (b) 0 ~ 0.6 V and (c) 0 ~ 1.3 V with [VRS] = 0.05 M and [TMPD] = 0.2 M.

Table S2. A partial list of electrochromic performance of ECDs containing viologens or TEMPO derivatives.

ECD system	λ_{max} (nm)	V_b/V_c[u] (V)	T_b/T_c (%)	ΔT[v] (%)	Ref.[w]
0.05 M HV[a] + 0.5 M $TBABF_4$[b] + 0.05 M TMPD in PC[c]	615	0/1.0	78.0/2.5	75.5	[42]
$PACV^{2+}$ [d]/ACN[e]:PC:PMMA[f]:$LiClO_4$ = 70:30:7:3/ITO	610	-2.0/2.0	90.5/51.0	39.5	[52]
TiO_2/viologen derivatives[g]/1 M $LiClO_4$ + 10 wt% PMMA in PC/PB[h]/ATO[i]	600	2.0/-2.0	67.3/0.2	67.1	[53]
PPBP[j]/PMMA–$EMIB(CN)_4$[k]–DMSO /PB	590	1.5/-1.5	82.3/34.5	47.8	[54]
RGO[l]/ 9 mM EV[m] + 9 mM HQ[n] + 2 M $BMIBF_4$[o] in PC/ RGO	600	0/1.5	-	27.0	[55]
HV + KCl in H_2O/PB	609	0/1.0	79.0/20.0	59.0	[56]
IBV[p]/P(HEMA)[q] + $EtMeIm^+N(CN)_2^-$ [r]/PB	605	0/-2.6	65.5/35	30.5	[57]
PB/PEG[s]:KPF_6:PC=5:20:100/ TEMPO-based polymer	700	-0.55/0	-	-	[46]
PV10-PSS[t]/PEG:KCl:DIW=5:10:100/ TEMPO-based polymer	550	-1.4/0.5	89.1/79.4	9.7	[58]
0.05 M VRS + 0.2 M TMPD in DMSO	620	0/0.4	75.2/12.6	62.6	This work

[a]Heptyl viologen; [b]Tetrabutylammonium tetrafluoroborate; [c]Propylene carbonate;
[d]Cross-linked matrix containing viologen; [e]Acetonitrile; [f]Poly(methyl methacrylate);
[g]1,4-bis[((N-Phosphono-2-ethyl)-4,4'-bipyridinium)-methyl]-benzene tetrachloride; [h]Prussian blue;
[i]Antimony tin oxide; [j]Poly-(cyclotriphosphazene-4,4'-bipyridinium)chloride; [k]1-ethyl-3-methylimidazolium tetracyanoborate
[l]Reduced graphene oxide; [m]Ethyl viologen; [n]Hydroquinone;
[o]1-methyl-3-butylimidazolium tetrafluoroborate; [p]1,1'-bis[4-(5,6-dimethyl-1H-benzimidazole-1-yl)butyl]-4,4'-bipyridinium dibromide
[q]Poly(2-hydroxyethyl methacrylate) [r]1-ethyl-3-methylimidazolium dicyanamide; [s]Polyethylene glycol;
[t]Polyion complex consisted of poly(decyl viologen) and poly(styrene sulfonate);
[u]V_b and V_c represent bleaching and coloring potential bias respectively.
[v]All transmittance changes listed here have included the absorbance of two conducting substrates.
[w]All the reference numbers in this table refers to that in the manuscript.

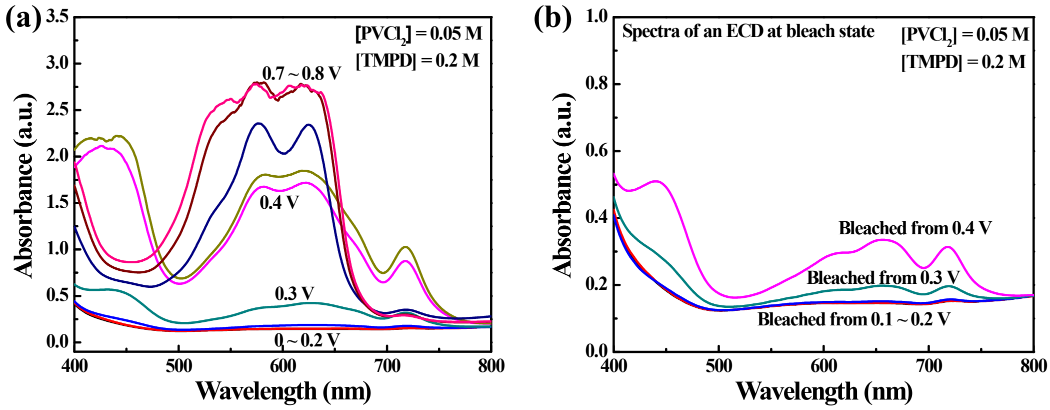

Figure S4. (a) The variation in the absorbance in response to the potential bias (0 to 0.8 V) for the ECD with [$PVCl_2$] = 0.05 M and [TMPD] = 0.2 M. (b) The absorbance of the ECD in the bleached state after applying coloring potential of 0.1 ~ 0.2 V, 0.3 V and 0.4 V.

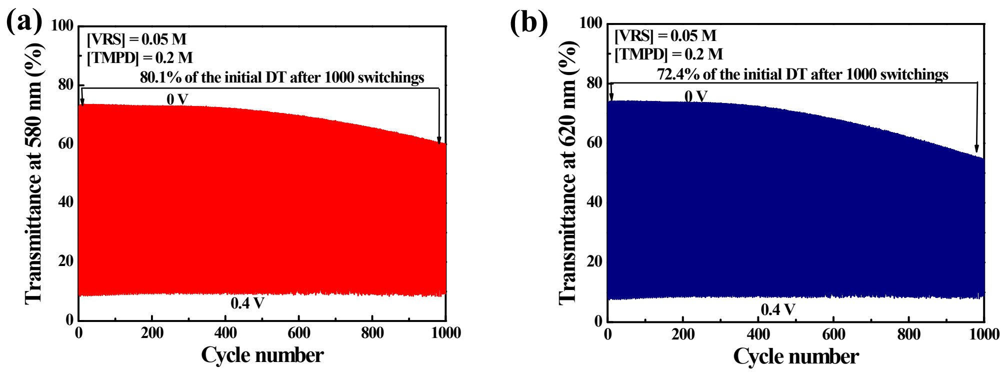

Figure S5. The variation in transmittance at (a) 580 and (b) 620 nm as a function of the cycle number of VRS/TMPD ECD for 1,000 cycles. The ECD was darkened at 0.4 V and bleached at 0 V with a coloring interval of 2 s and a bleaching interval of 25 s.