Electronic Supplementary Information

Electrochromic triphenylamine-based cobalt(II) complex nanosheets

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Synthesis of ligands

Synthesis of L1



Scheme S1a. Synthetic route for L1.

Tris(4-bromophenyl)amine was prepared through the reported procedure^[1] and then it was used to synthesize tris(4-formylphenyl)amine.^[2] L1 was synthesized based on the modified literature procedure.^[3] To tris(4-formylphenyl)amine (200.0 mg, 0.6 mmol), 2-acetylpyridine (484.6 mg, 4.0 mmol) and sodium hydroxide (195.2 mg, 4.9 mmol) were added to grind them together with mortar and pestle. When a yellow solid was formed, which means the completion of aggregation, the solid was transferred into a flask and suspended into ethanol (19 mL). After stirring at room temperature (r.t.) for 2 h, NH₄OH solution (19 mL, 28% - 30%) was added and then the system was warmed to reflux for 20 h. The precipitate was filtered and washed with ethanol. After

crystallization from ethanol, aluminum oxide column chromatography eluting with dichloromethane was employed for further purification of the product. A yellow solid was obtained (152.1 mg, 27%). ¹H NMR (400 MHz, CDCl₃, δ): 8.76 (s, 6H, Py- $H^{3',5'}$), 8.75 (d, 6H, Py- $H^{6,6''}$), 8.70 (d, 6H, Py- $H^{3,3''}$), 7.91-7.89 (m, 12H, Py- $H^{4,4''}$, Ar-H), 7.38-7.32 (m, 12H, Py- $H^{5,5''}$, Ar-H); ¹³C NMR (400 MHz, CDCl₃, δ): 156.4, 155.9, 149.7, 149.2, 136.9, 128.5, 128.3, 124.5, 123.8, 121.9, 121.4, 118.5, 118.4; MALDI-TOF-MS (*m*/*z*): [M+H]⁺ calculated for C₆₃H₄₃N₁₀, 939.36; found, 939.31.

Synthesis of L2



Scheme S1b. Synthetic route for L2.

Tris(4-formylbiphenyl)amine was synthesized according to the modified procedure.^[4] **L2** was synthesized similarly as described above for **L1** except that tris(4formylbiphenyl)amine was used instead of tris(4-formylphenyl)amine. Tris(4formylbiphenyl)amine (0.52 g, 0.90 mmol), 2-acetylpyridine (0.74 g, 6.0 mmol), NaOH (0.30 g, 7.5 mmol), aqueous NH₃.H₂O (80 mL) and ethanol (80 mL) were used to afford a white solid (273 mg, 26%). ¹H NMR (400 MHz, CDCl₃, δ): 8.82 (s, 6H, Py- $H^{3',5'}$), 8.75 (d, 6H, Py- $H^{6,6''}$), 8.70 (d, 6H, Py- $H^{3,3''}$), 8.02 (d, 6H, Ar-H), 7.90 (dt, 6H, Py- $H^{4,4''}$), 7.78 (d, 6H, Ar-H), 7.65 (d, 6H, Ar-H), 7.37 (m, 12H, Py- $H^{5,5''}$), 7.32 (d, 6H, Ar-H); ¹³C NMR (400 MHz, CDCl₃, δ): 156.3, 156.0, 149.8, 149.2, 147.1, 141.2, 136.9, 134.9, 130.4, 128.0, 127.8, 127.1, 124.6, 123.9, 121.4, 118.7; MALDI-TOF-MS (m/z): [M+H]⁺ calculated for C₈₁H₅₅N₁₀, 1167.46; found, 1167.46.



Fig. S1a. The ¹H NMR spectrum of L1 in CDCl₃.



Fig. S1b. The ¹H NMR spectrum of L2 in CDCl₃.



Fig. S2. Photograph of a series of **Co-S1** prepared at the interfaces using containers with diameters of 58 mm, 70 mm and 88 mm, respectively.



Fig. S3. The SEM image of **Co-S1** deposited on the Si substrate. There are three regions with different contrasts. The bare Si and nanosheet-covered area are marked, respectively. The middle part between the Si and **Co-S1** corresponds to the doubly folded **Co-S1**.



Fig. S4. The effects of a) reaction time on the thickness of **Co-S1**. The concentration of ligand and metal ion were fixed to be 0.05 mM and 25 mM, respectively. b) the ligand concentration on the thickness of **Co-S1**. The concentration of metal ion was fixed to be 25 mM and the reaction lasted for 3 weeks. c) the concentration of Co^{2+} ion on the thickness of **Co-S1**. The ligand concentration was fixed to be 0.05 mM and

the reaction lasted for 3 weeks.



Fig. S5. The FTIR spectra of a) Co-S1 and L1; b) Co-S2 and L2.



Fig. S6. a) The chemical structure of the referential complex R. The full XP spectra ofb) R; c) L1; d) Co-S1; e) L2; f) Co-S2.



Fig. S7. The mechanical strength of a) **Co-S1** and b) **Co-S2**. The original nanosheets suspended in EtOH/CH₂Cl₂ solution. Then, the sheets were clamped with a tweezer. They were curled after being totally exposed to air but could recover again after being immersed into the solution.



Fig. S8. TGA results for a) Co-S1 and b) Co-S2.



Fig. S9. The electrochemical performance of **Co-S1**. a) The plots of $i_{pa}-v^{1/2}$ and $i_{pc}-v^{1/2}$. i_{pa} is the anodic peak current while i_{pc} is the cathodic peak current. v is the scan rate. b) The double potential-step chronocoulomogram. The initial potential was set at -0.2 V and high potential was set at 1.8 V and each step lasted for 10 s. c) The current-time profile of **Co-S1** at the constant potential of 1.8 V for 100 s. d) The multiple CV scan results with the scan speed of 1 V s⁻¹. e) The corresponding charge-time response curve. f) The electrochromic stability measurement with repetitive double potential-step chronocoulometry between potential of -0.1 V and 2.0 V and each step lasted for 5 s.



Fig. S10. a) The potential-step chronocoulomogram of **Co-S2**. The parameter was set at the initial potential of 0 V, high potential of 2.5 V, step number of 2 and width of 5 s. b) The plots of $i_{pa}-v^{1/2}$ and $i_{pc}-v^{1/2}$. i_{pa} is the anodic peak current while i_{pc} is the cathodic peak current. v is the scan rate. c) The current-time profile of **Co-S2** at a constant potential of 2.5 V for 100 s. d) The electrochromic stability measurement with repetitive double potential-step chronocoulometry between 0 V and 1.8 V and each step lasted for 5 s.



Fig. S11. The electrochromic stability measurement for **Co-S1** based device with repetitive double potential-step chronocoulometry between -0.5 V and 2.5 V and each step lasted for 10 s.

The effects of reaction time, ligand concentration and Co²⁺ concentration on the thickness of the nanosheet Co-S1

The surface profiler was used to measure the thickness of a series of **Co-S1** on Si substrates. On each sample, five testing points were evenly chosen to carry out the cross-sectional analysis and then the average value of each sample was also calculated.

Table S1 Effect of reaction time on the thickness of Co-S1

Reaction	Tha 1 / nm	Th $2/nm$	Th $2/nm$	Th $4/nm$	Th $5/nm$	Th b/nm
time	111"-1 / 11111	111-2 / 11111	111-3 / 11111	111-4 / 11111	111-3 / 11111	I II _{ave} / IIIII
24 h	33	34	30	36	33	33
72 h	141	139	140	136	137	139
1 week	261	252	258	255	260	257
3 weeks	260	262	265	263	264	263
5 weeks	288	282	281	286	282	284

 ${}^{a}Th =$ thickness of the selected area of the nanosheet. The suffix number means the different selected area. ${}^{b}Th_{ave} =$ average of the series of thickness values.

Ligand						
concentration	Th-1 / nm	Th-2 / nm	Th-3 / nm	Th-4 / nm	Th-5 / nm	Th _{ave} / nm
/ mM						
0.01	39	39	42	40	39	40
0.025	125	126	122	123	125	124
0.05	264	293	284	280	274	279
0.1	510	504	504	505	506	506
0.2	1131	1122	1108	1117	1126	1121

Table S2 Effect of ligand concentration on the thickness of Co-S1

Concentration						
of Co ²⁺	Th-1 / nm	Th-2 / nm	Th-3 / nm	Th-4 / nm	Th-5 / nm	Th_{ave} / nm
solution / mM						
5	183	185	179	182	183	182
10	231	228	229	229	230	229
20	237	245	244	243	240	242
25	285	291	285	285	283	286
50	296	291	306	308	300	300

Table S3 Effect of Co²⁺ concentration on the thickness of Co-S1

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