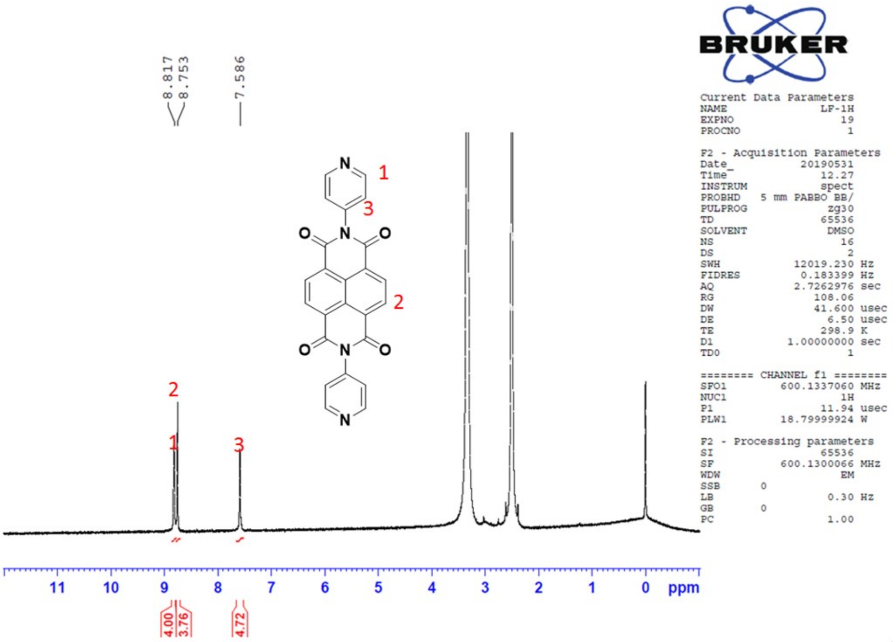
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

1. Synthesis of N,N′-di(4-pyridyl)-1,4,5,8-naphthalene diimide

N,N′-Di(4-pyridyl)-1,4,5,8-naphthalene diimide (DPNDI) was synthesized according to previous methods with some modifications.[1] 1,4,5,8-Naphthalenetetracarboxylic dianhydride (1.20 g; 4.5 mmol), 4-aminopyridine (1.10 g; 11.3 mmol), and dry DMF (50 mL) were refluxed for 2 h. After cooling to room temperature, the reaction mixture was filtered, and the filter cake was washed with cold DMF, water, acetone, and CH_2Cl_2 (50 mL of each). DPNDI as a gray-white solid was obtained by recrystallization with DMF. Yield: 1.31 g, 69%. ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 8.82 (s, 4H), 8.75 (s, 4H), 7.59 (s, 4H).[1]



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F2 - Processing parameters
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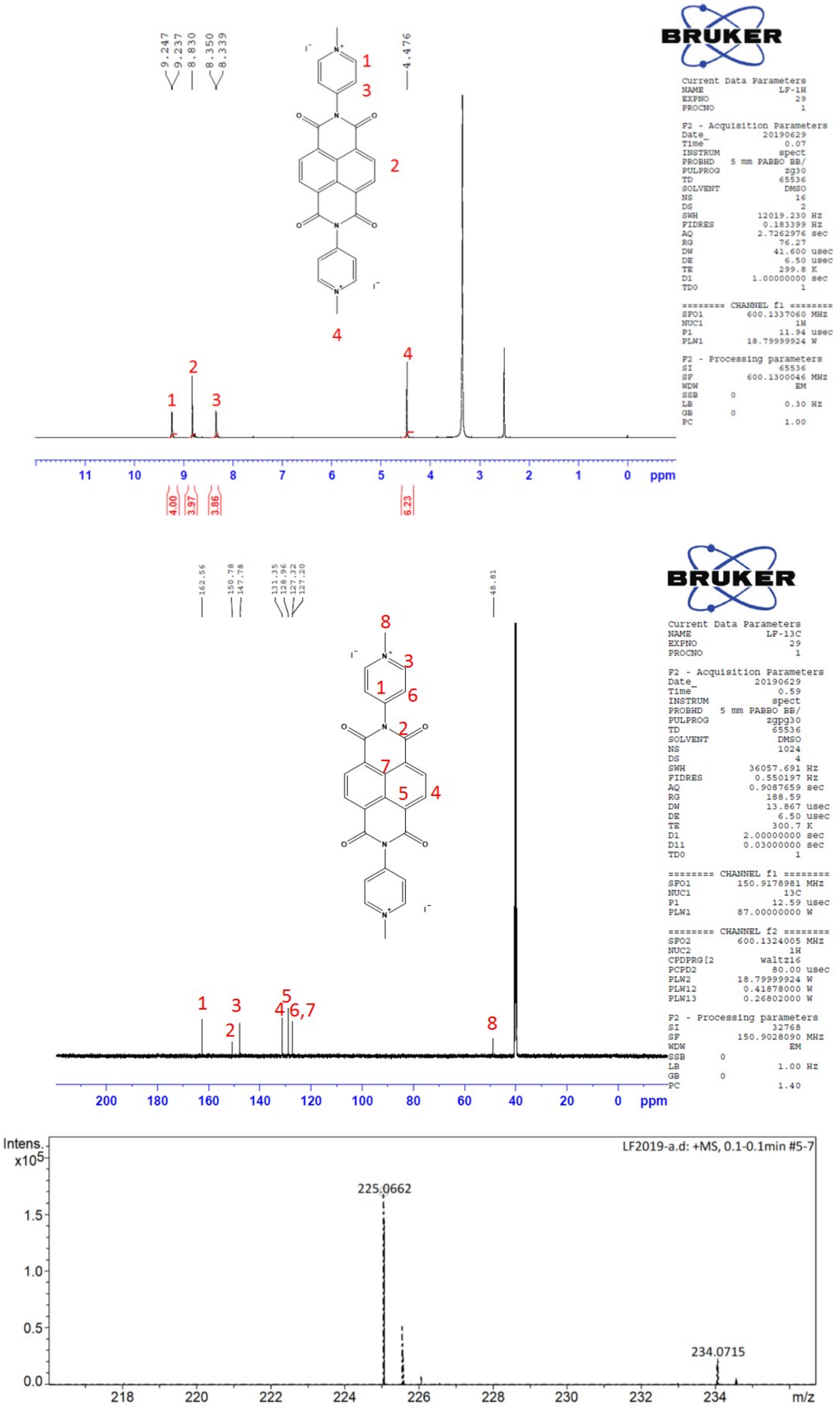
Fig. S1 ^{1}H NMR of DPNDI.

2. Synthesis of $(Me_2DPNDI)^{\cdot}(2I)$ and $(Benzyl_2DPNDI)^{\cdot}(2Br)$

$(Me_2DPNDI)^{\cdot}(2I)$ and $(Benzyl_2DPNDI)^{\cdot}(2Br)$ were synthesized according to the method reported by Huang's group[2] with some modifications. DPNI (0.50 g, 1.2 mmol) was dissolved in a mixed solution of acetonitrile and DMF (1:1, v/v), to which RX (4.8 mmol) solution in acetonitrile was added dropwise. The resultant mixture was refluxed for 24 h, and then cooled to room temperature. After filtration and subsequent washing with dichloromethane, the desired product was obtained by recrystallization from methanol/water for $(Me_2DPNDI)^{\cdot}(2I)$ and methanol for $(Benzyl_2DPNDI)^{\cdot}(2Br)$.



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FIDRES         0.550197 Hz
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RG               188.59
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DE                 6.50 usec
TE                300.7 K
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D11          0.03000000 sec
TD0                   1

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NUC1                13C
P1                12.59 usec
PLW1        87.00000000 W

======== CHANNEL f2 ========
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NUC2                 1H
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PCPD2             80.00 usec
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PLW12        0.41878000 W
PLW13        0.26802000 W

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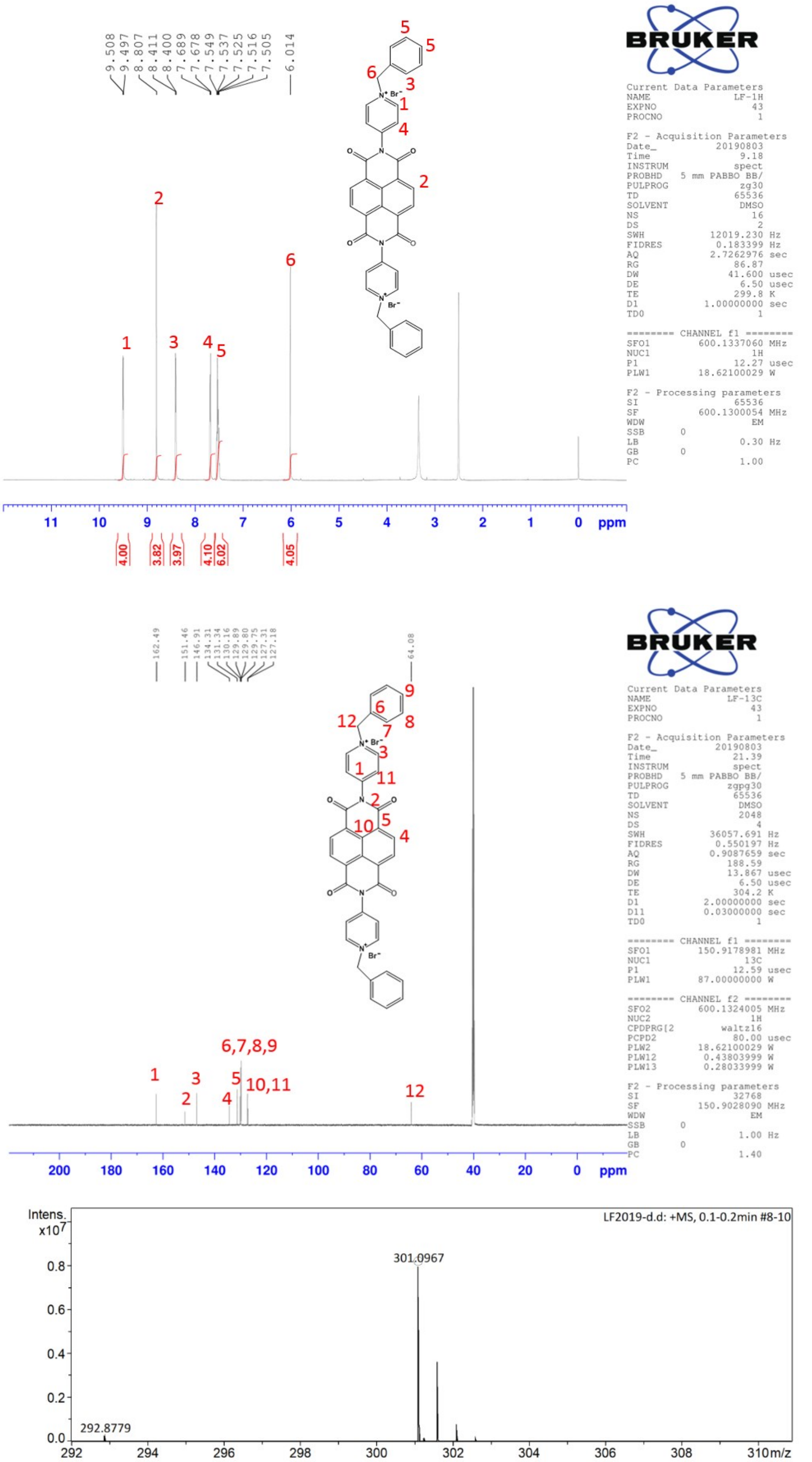
Fig. S2 ^{1}H NMR (top), ^{13}C NMR (middle), and HRMS (bottom) of (Me$_2$DPNDI)$^·$(2I).



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TE                   299.8 K
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TD0                      1

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NUC1                    1H
P1                   12.27 usec
PLW1           18.62100029 W

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PROCNO                   1

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DS                       4
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FIDRES            0.550197 Hz
AQ               0.9087659 sec
RG                  188.59
DW                  13.867 usec
DE                    6.50 usec
TE                   304.2 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
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NUC1                   13C
P1                   12.59 usec
PLW1           87.00000000 W

======== CHANNEL f2 ========
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NUC2                    1H
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PCPD2                80.00 usec
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PLW12           0.43803999 W
PLW13           0.28033999 W

F2 - Processing parameters
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WDW                     EM
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LB                    1.00 Hz
GB        0
PC                    1.40
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Fig. S3 ^{1}H NMR (top), ^{13}C NMR (middle), and HRMS (bottom) of (Benzyl$_2$DPNDI)$^{\cdot}$(2Br).

3. Cyclic voltammetry

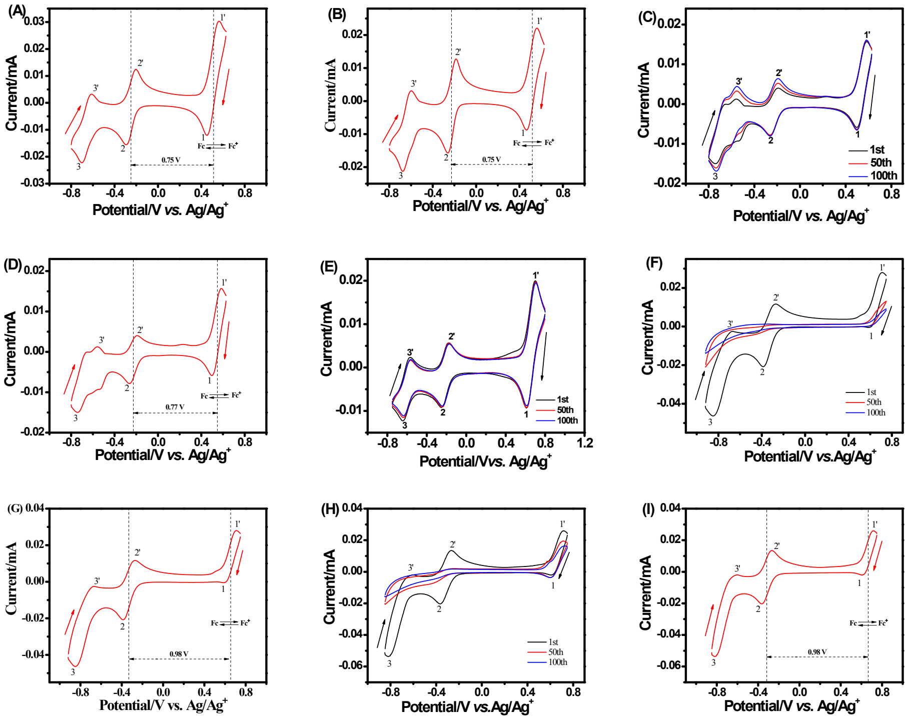

Fig. S4 CV analysis of compounds ($(Me_2DPNDI)\bullet(2I)$) (A), ($(Benzyl_2DPNDI)\bullet(2Br)$) (B), NDA (C, D), and DPNDI (E), (1.0 mM) and Fc in DMSO/TBAP (50 mM) and compound 1 (F, G) and compound 2 (G, H) in NMP/TBAP vs Ag/Ag$^+$ at room temperature and a scan rate of 50 mV s^{-1} upon purging N_2.

4. Coloration efficiency

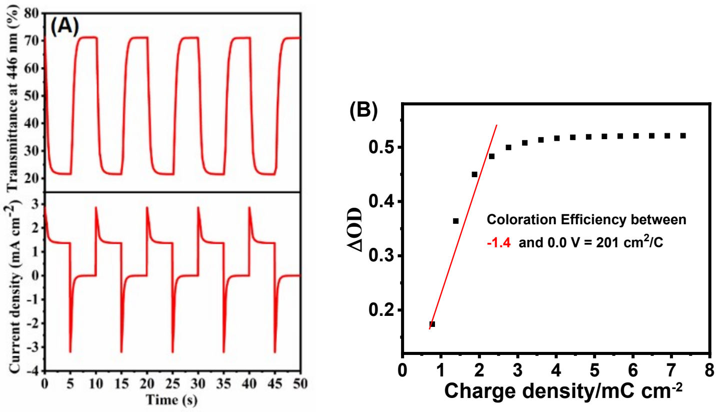

Fig. S5 Chronoamperometry curves and the corresponding in-situ transmittance curve (A) and the optical density versus charge density (B) of the ECDs based on NDA between −1.4 and 0.0 V.

5. Spin density

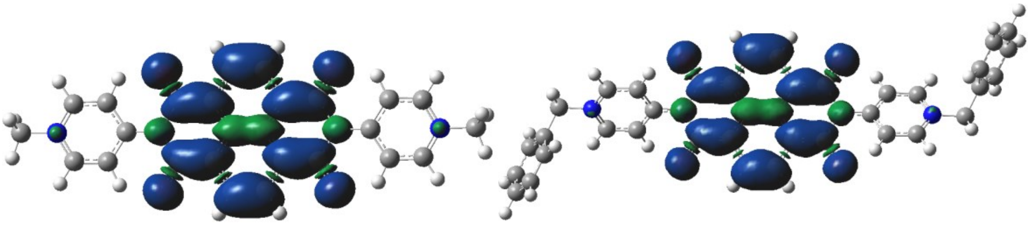

Fig. S6 Spin density of radical-cation species of (Me$_2$DPNDI)●(2I) (left) and (Benzyl$_2$DPNDI)●(2Br) (right).

6. Long-life performance

In order to investigate the long-life performance of (Me$_2$DPNDI)●(2I) and (Benzyl$_2$DPNDI)●(2Br), the change in spectroelectrochemistry and color of the ECDs based on (Me$_2$DPNDI)●(2I) and (Benzyl$_2$DPNDI)●(2Br) were investigated by keeping (Me$_2$DPNDI)●(2I) and (Benzyl$_2$DPNDI)●(2Br) in its colored state at an applied voltage of -1.4 V for different times. The result was shown Fig. S7. For the ECD based on (Me$_2$DPNDI)●(2I) (Fig. S7A), after it was kept at its colored state for 12 h (43200 s), no obvious change in UV-Vis spectroelectrochemistry was observed, and the colored state slightly become lighter after 9 h. There was no apparent degradation after 8640 cycles. For the ECD based on

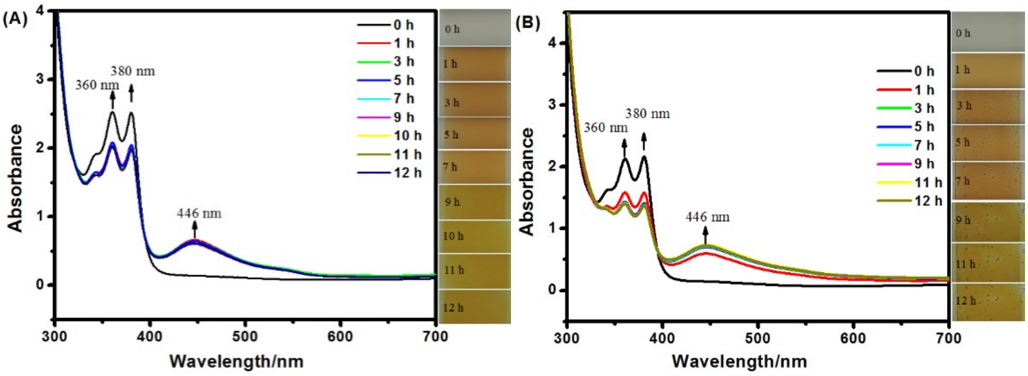

Fig. S7 UV-Vis absorption spectra for ECDs based on (Me$_2$DPNDI)●(2I) (A) and (Benzyl$_2$DPNDI)●(2Br) (B) at an applied DC voltages of −1.4 V for different time and the corresponding photographs of coloured states.

($Benzyl_2DPNDI$)●(2Br) (Fig. S7B), the adsorption intensity at 446 nm slightly increased after 3 h (10800 s), at the same time, some particles appeared and the ECD began to age. The colored state slightly become lighter after 9 h. This indicated that (Me_2DPNDI)●(2I) performs better.

7. Synthesis and electrochromic properties characterization of NDI derivatives

Two NDI derivatives, 2,7-dibutylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (compound 1) and 2,7-diphenylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (compound 2), were synthesized according to previous methods.[3] NDA (0.50 g, 1.86 mmol) was dissolved in solution of DMF, to which appropriate amine (4.48 mmol) was added dropwise and heated to 130 ^{o}C for 8 h. The reaction mixture was cooled to room temperature. The crude product was collected by filtration, and the final product was obtained by recrystallization with DMF.

2,7-Dibutylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (compound 1), grayish-white crystalline, yield: 0.44 g, 63%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.75 (s, 4H), 4.20 (t, 4H, J = 7.2-15.0 Hz), 1.71-1.75 (m, 4H), 1.44-1.48 (m, 4H), 0.99 (t, 6H, J = 7.2-14.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 162.8, 130.9, 126.7, 126.6, 40.7, 30.2, 20.3, 13.7.

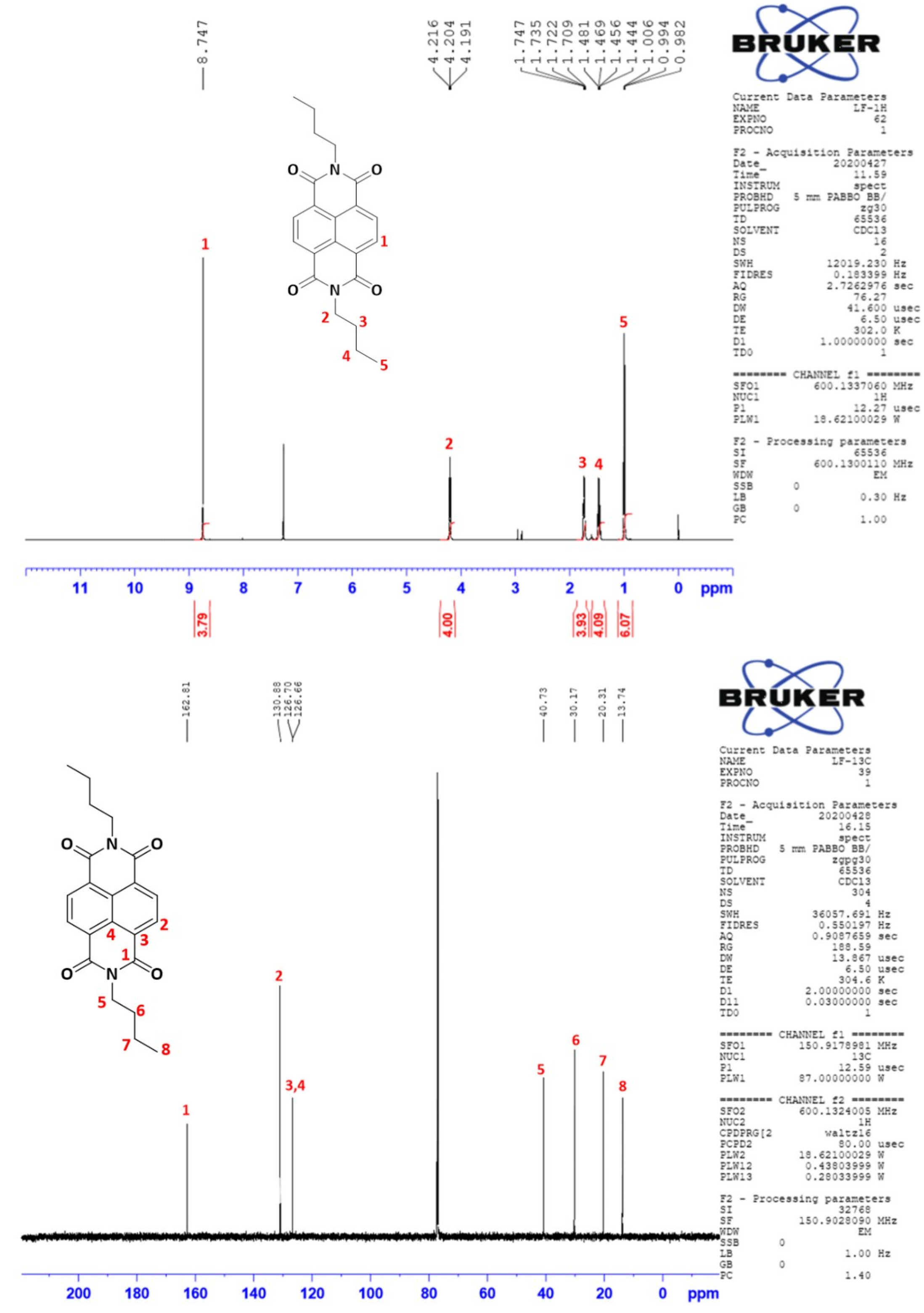

Fig. S8 ^{1}H NMR (top) and ^{13}C NMR (bottom) of compound 1.

2,7-Diphenylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (compound 2), pale brown crystalline, yield: 0.56 g, 72%. ^{1}H NMR (600 MHz, DMSO-d_6) δ(ppm):

8.72 (s, 4H), 7.57 (t, 4H, J = 7.8-15.0 Hz), 7.50 (t, 2H, J = 7.2-15.0 Hz), 7.47 (d, 4H, J = 7.2 Hz). ^{13}C NMR (150 MHz, DMSO-d$_6$) δ (ppm): 163.4, 136.1, 130.9, 129.5, 129.4, 129.0, 127.5, 127.2.

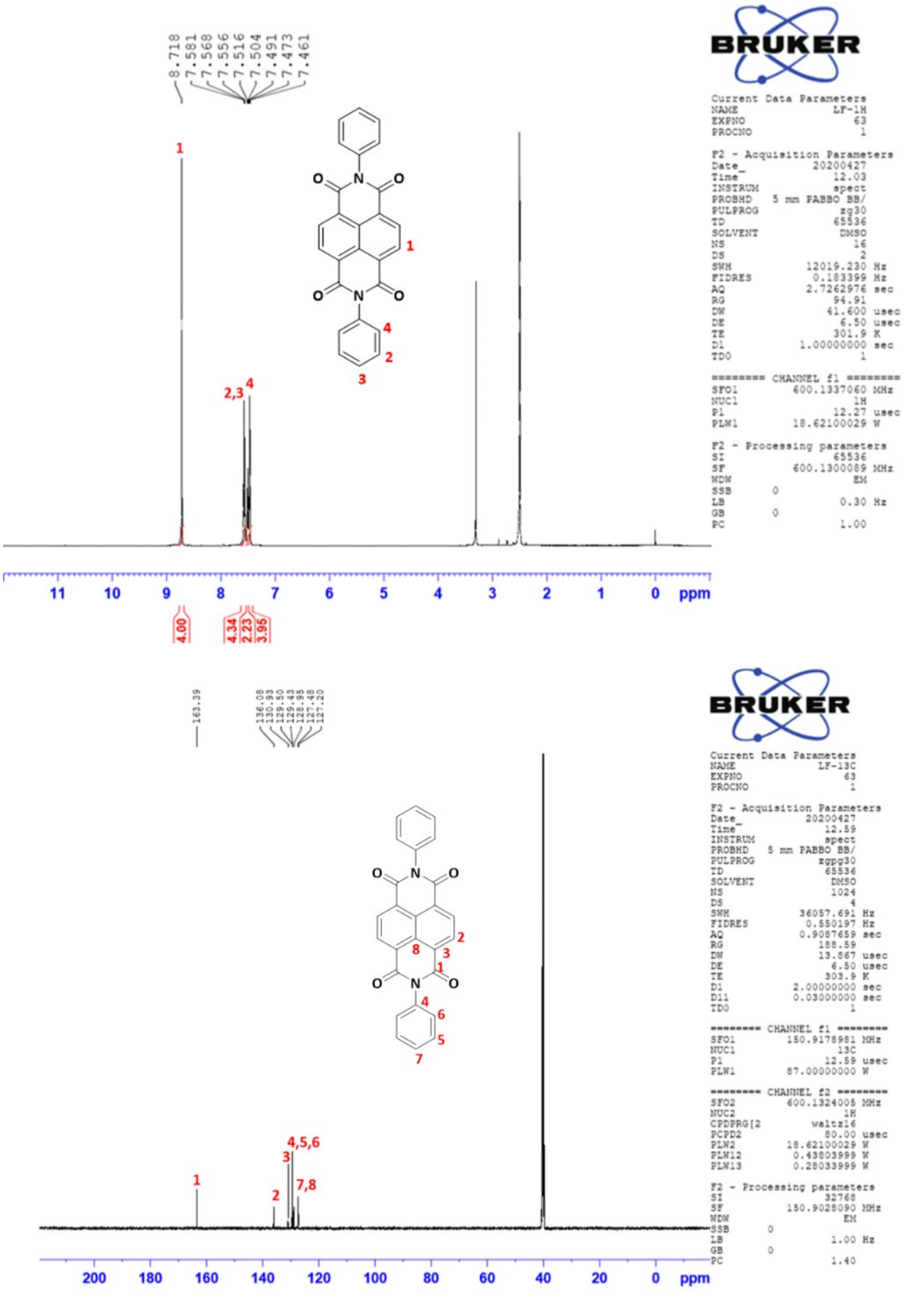

Fig. S9 ^{1}H NMR (top) and ^{13}C NMR (bottom) of compound 2.

Sandwich-type ECDs (30 mm × 30 mm × 0.035 mm) based on compounds 1 and 2 were constructed using glass coated with indium tin oxide (ITO) and a reflective metal surface (50 Ω / sq) as the electrodes. Compound 1/compound 2

(20 mM), ferrocene (20 mM), and tetrabutylammonium perchlorate (20 mM) were dissolved in N-methyl-2-pyrrolidone due to poor solubility of compounds 1 and 2 in DMSO. The resultant solution was injected into the interlayer of two ITO glasses with a syringe.

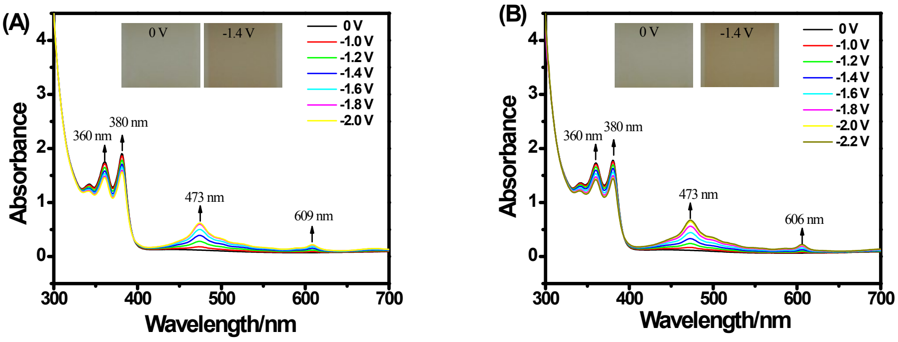

Fig. S10 UV-Vis absorption spectra for ECDs based on compounds 1 (A) and 2 (B) at different DC voltages (Inset: Photographs of the devices in their bleached and colored states under applied DC voltages of 0.0 V and −1.4 V, respectively).

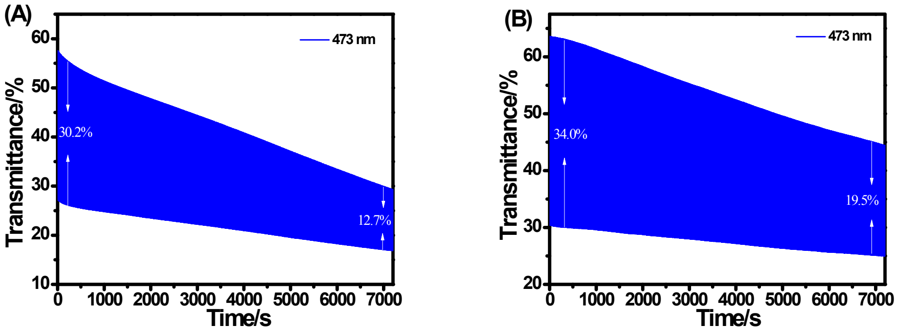

Fig. S11 Electrochromic switching responses of ECDs monitored at 473 nm between −1.4 and 0.0 V for compounds 1 (A) and 2 (B).

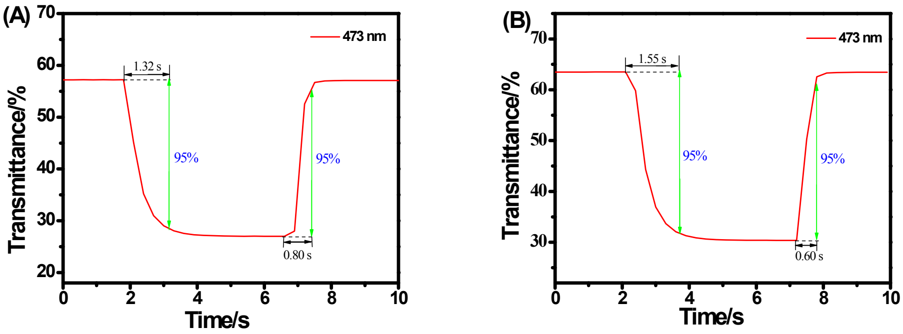

Fig. S12 Response times of ECDs based on compounds 1 (A) and 2 (B) between −1.4 and 0.0 V.

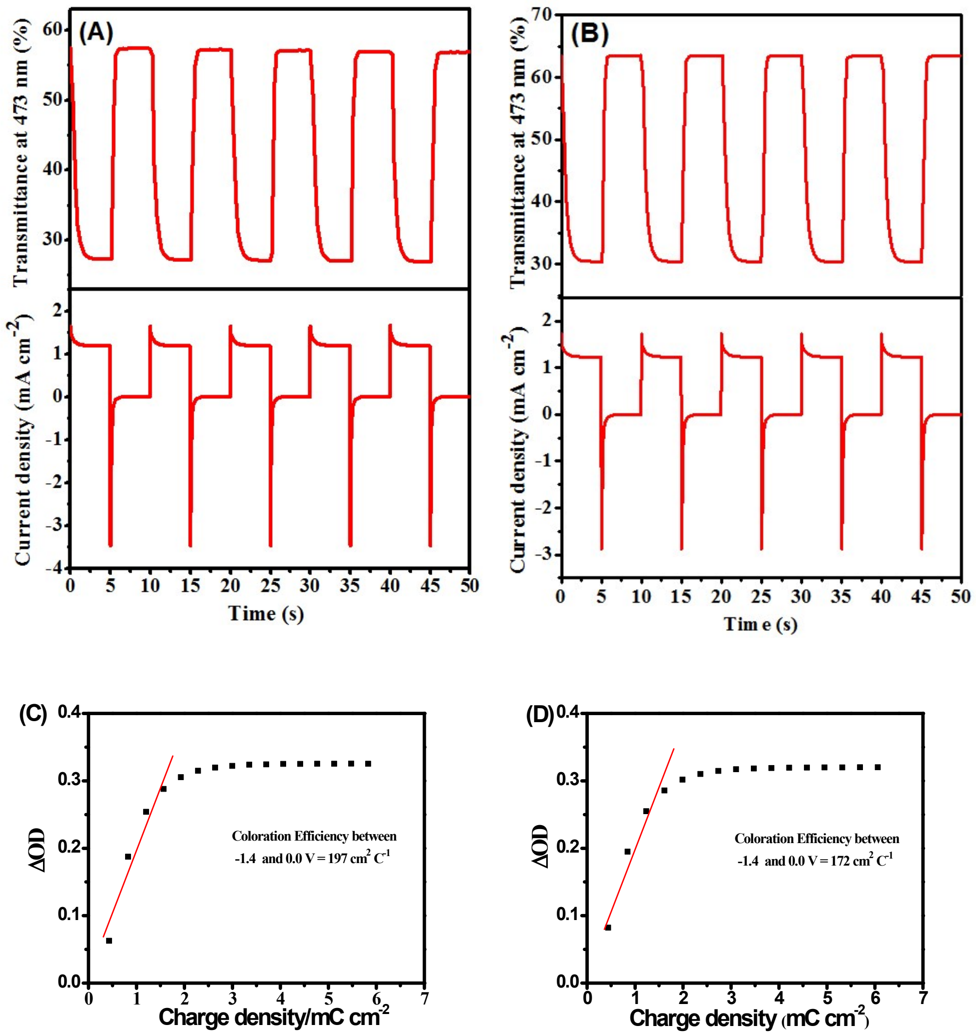

Fig. S13 Chronoamperometry curves and the corresponding in-situ transmittance curve and the optical density versus charge density of the ECDs based on compounds 1 (A, C) and 2 (B, D) between −1.4 and 0.0 V.

8. Transmittance spectra

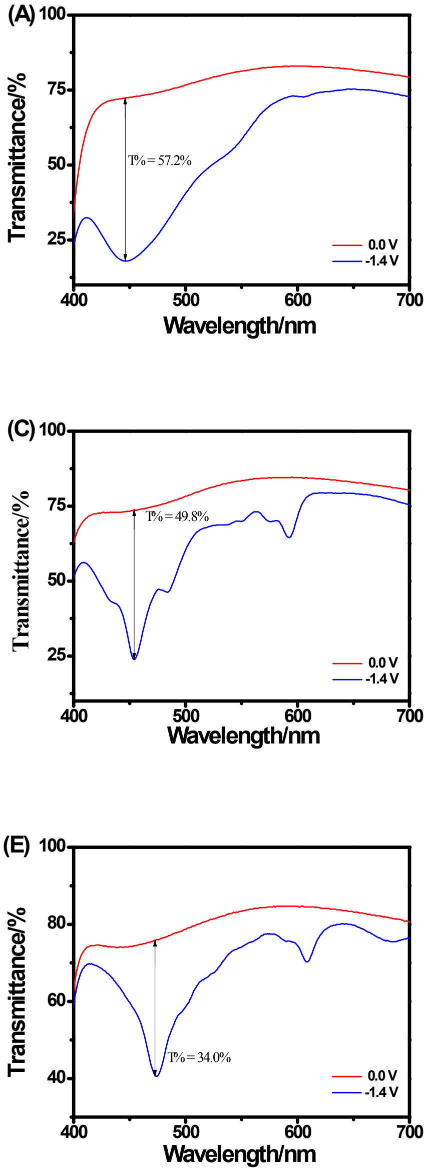

Fig. S14 The transmittance spectra of ECDs based on (Me_2DPNDI)●(2I) (A), ($Benzyl_2$DPNDI)●(2Br) (B), NDA (C), compound 1 (D), and compound 2 (E) in the bleached (red line) and the colored states (blue line).

References

1 S. Mukherjee, R. Babarao, A. V. Desai, B. Manna and S. K. Ghosh, *Crystal Growth & Design*, 2017, **17**, 3581-3587.

2 J. J. Liu, Y. F. Guan, C. Jiao, M. J. Lin, C. C. Huang and W. X. Dai, *Dalton Transactions*, 2015, **44**, 5957-5960.

3 S. Maniam, S. Sandanayake, E. I. Izgorodina and S. J. Langford, Asian Journal of Organic Chemistry, 2016, **5**, 490-493.