Supplementary Information (SI) for New Journal of Chemistry.

Supplementary Information

Aggregation-enhanced emission and multicolored electrochromic behavior of polyphenyl benzoates

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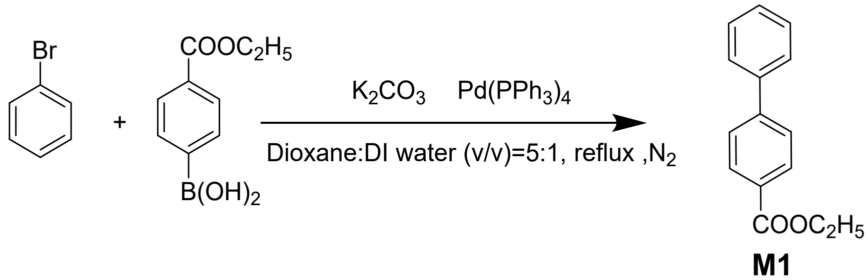
S1. Synthesis and characterization of polyphenyl benzoates (M1–M5)

Synthesis of M1

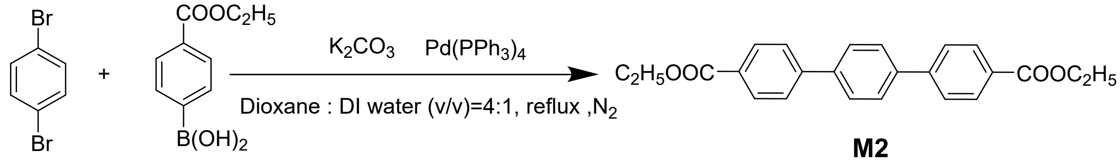


M1

Scheme S1. Synthesis of 1,1′-biphenyl]-4-carboxylic acid, ethyl ester (**M1**).

Bromobenzene (1.50 g, 9.55 mmol), 4-ethoxycarbonylphenylboronic acid (2.78 g, 14.33 mmol, 1.5 eq.), and potassium carbonate (3.96 g, 28.65 mmol, 3.0 eq.) were dissolved in 50 mL of a mixed solvent of 1,4-dioxane and deionized water (DI water) (v/v, 5/1). After the reactant mixture was bubbled with nitrogen for 20 min, 5% tetrakis (triphenylphosphine) palladium (0) (0.55 g, 0.48 mmol, 0.05 eq) was quickly added and heated in a nitrogen atmosphere to reflux at 85 °C for 48 h. The reaction mixture was cooled to room temperature, extracted with dichloromethane, washed with water and dried with anhydrous magnesium sulfate. A colorless flake crystal **M1** (1.21 g) was obtained with a yield of 56% after purification by silica gel chromatography column with petroleum ether/ethyl acetate (v/v, 100/1) as the eluent, and dried in a vacuum oven at 60 °C. M. p.: 40.8–42.0 °C. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.11 (d, J = 8.4 Hz, 2H), 7.66 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.46 (t, J = 7.8 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 4.41 (q, 2H), 1.41 (t, J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.49, 145.55, 140.12 130.05, 129.34, 128.89, 128.08, 127.27, 126.99, 60.92, 14.34. HRMS (ESI) ($CHCl_3$, positive mode): m/z for $C_{15}H_{15}O_2$ $[M+H]^+$: calculated: 227.1065, found: 227.1067.

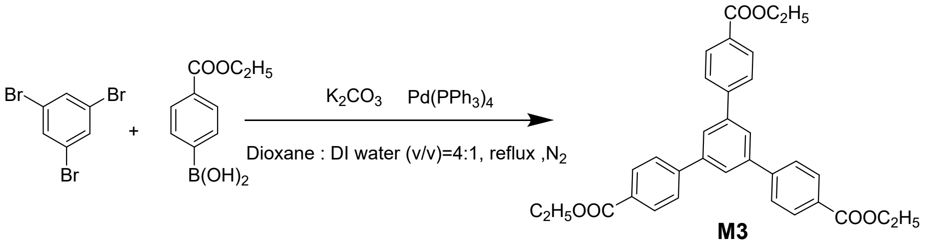
Synthesis of M2



Scheme S2. Synthesis of diethyl [1,1':4',1''-terphenyl]-4,4''-dicarboxylate (**M2**).

1,4-Dibromobenzene (2.00 g, 8.48 mmol), 4-ethoxycarbonylphenylboronic acid (4.93 g, 25.43 mmol, 3.0 eq.), and potassium carbonate (7.03 g, 50.87 mmol, 6.0 eq.) were dissolved in 50 mL of a mixed solvent of 1,4-dioxane and DI water (v/v, 5/1). After the reactant mixture was bubbled with nitrogen for 20 min, 5% tetrakis (triphenylphosphine) palladium (0) (0.49 g, 0.42 mmol, 0.05 eq) was quickly added and heated in a nitrogen atmosphere to reflux at 85 °C for 48 h. The reaction mixture was cooled to room temperature, extracted with dichloromethane, washed with water and dried with anhydrous magnesium sulfate. A colorless flake crystal **M2** (1.64 g) was obtained with a yield of 52% after recrystallization from dichloromethane, and dried in a vacuum oven at 60 °C. M. p.: 183.0–184.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.14 (d, J = 7.8 Hz, 4H), 7.71 (t, J = 7.8 Hz, 8H), 4.41 (q, 4H), 1.42 (t, J = 7.2 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.41, 144.75, 139.82, 130.14, 129.61, 127.77, 126.89, 60.96, 14.33. HRMS (ESI) ($CHCl_3$, positive mode): m/z for $C_{24}H_{23}O_4$ $[M+H]^+$: calculated: 375.1590, found: 375.1591.

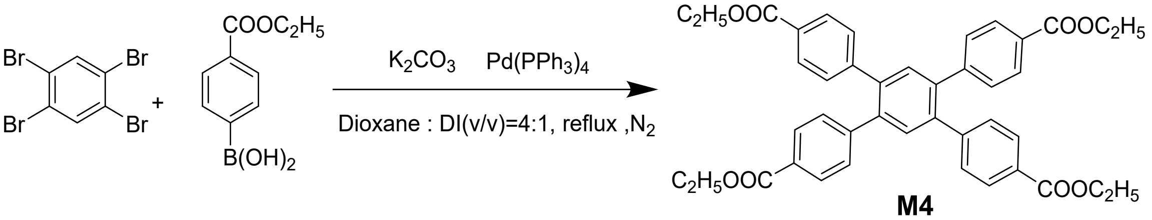
Synthesis of M3



Scheme S3. Synthesis of diethyl 5'-(4-(ethoxycarbonyl)phenyl)-[1,1':3',1''-terphenyl]- 4,4''-dicarboxylate (**M3**).

1,3,5-Tribromobenzene (1.81 g, 5.75 mmol), 4-ethoxycarbonylphenylboronic acid (5.02 g, 25.87 mmol, 4.5 eq.), and potassium carbonate (7.15 g, 51.75 mmol, 9.0 eq.) were dissolved in 50 mL of a mixed solvent of 1,4-dioxane and DI water (v/v, 5/1). After the reactant mixture was bubbled with nitrogen for 20 min, 5% tetrakis (triphenylphosphine) palladium (0) (0.33 g, 0.29 mmol, 0.05 eq) was quickly added and heated in a nitrogen atmosphere to reflux at 85 °C for 4 days. The reaction mixture was cooled to room temperature, extracted with dichloromethane, washed with water and dried with anhydrous magnesium sulfate. A colorless flake crystal **M3** (1.73 g) was obtained with a yield of 58% after recrystallization from dichloromethane, and dried in a vacuum oven at 60 °C. M. p.: 188.6–189.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.17 (d, J = 7.8 Hz, 6H), 7.86 (s, 3H), 7.76 (d, J = 7.8 Hz, 6H), 4.43 (q, 6H), 1.43 (t, J = 7.2 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.33, 144.92, 141.71, 130.21, 129.94, 127.23, 126.01, 61.03, 14.33. HRMS (ESI) ($CHCl_3$, positive mode): m/z for $C_{33}H_{30}O_6$ $[M+H]^+$: calculated: 523.2124, found: 523.2115.

Synthesis of M4

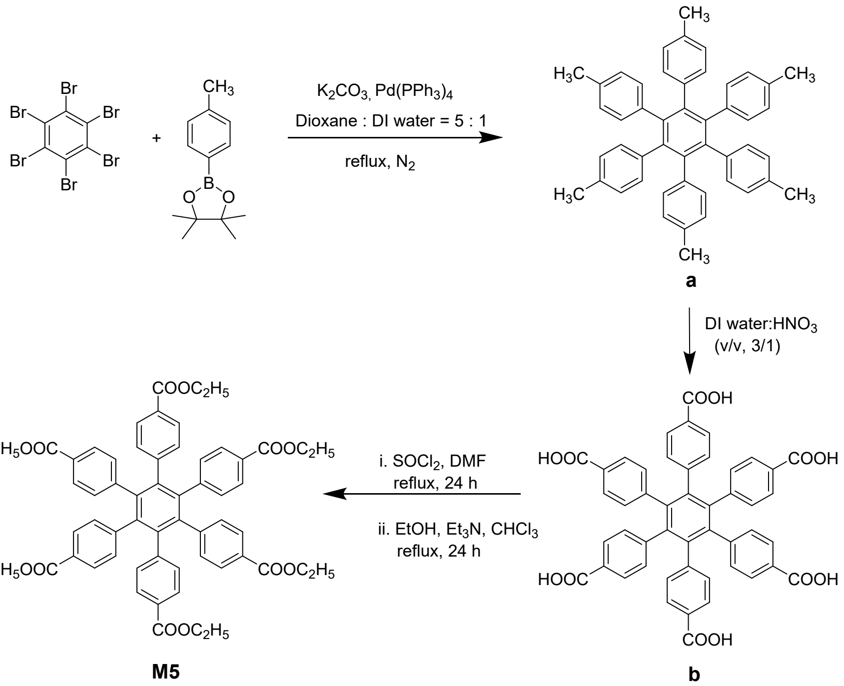


Scheme S4. Synthesis of diethyl 4',5'-bis(4-(ethoxycarbonyl)phenyl)-[1,1':2',1''-terphenyl]- 4,4''-dicarboxylate (**M4**).

1,2,4,5-Tetrabromobenzene (2.10 g, 5.33 mmol), 4-ethoxycarbonylphenylboronic acid (6.21 g, 32.00 mmol, 6 eq.), and potassium carbonate (8.85 g, 64.00 mmol, 12 eq.) were dissolved in a mixed solvent of 1,4-dioxane and DI water (50 mL v/v, 5/1). After the reactant mixture was bubbled with nitrogen for 20 min, 5% tetrakis (triphenylphosphine) palladium (0) (0.31 g, 0.27 mmol, 0.05 eq.) was quickly added and heated in a nitrogen atmosphere to reflux at 85 °C for 72 h. The reaction mixture was cooled to room temperature, extracted with dichloromethane, washed with water, and dried with anhydrous magnesium sulfate. A white solid **M4** (1.58 g) was obtained with a yield of 44% after purified by silica gel chromatography column with petroleum ether/ethyl acetate (v/v, 10/1) as the eluent, and dried in a vacuum oven at 60 °C. M. p.: 231.1–232.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.93 (d, J = 7.8 Hz, 8H), 7.55 (s, 2H), 7.26 (d, J = 3.6 Hz, 8H), 4.39-

4.35 (m, 8H), 1.39 (t, *J* = 6.6-13.8 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.32, 144.78, 139.53, 132.74, 129.76, 129.49, 129.25, 61.02, 14.31. HRMS (ESI) ($CHCl_3$, positive mode): m/z for $C_{42}H_{38}O_8$ $[M+Na]^+$: calculated : 693.2459, found : 693.2463.

Synthesis of M5

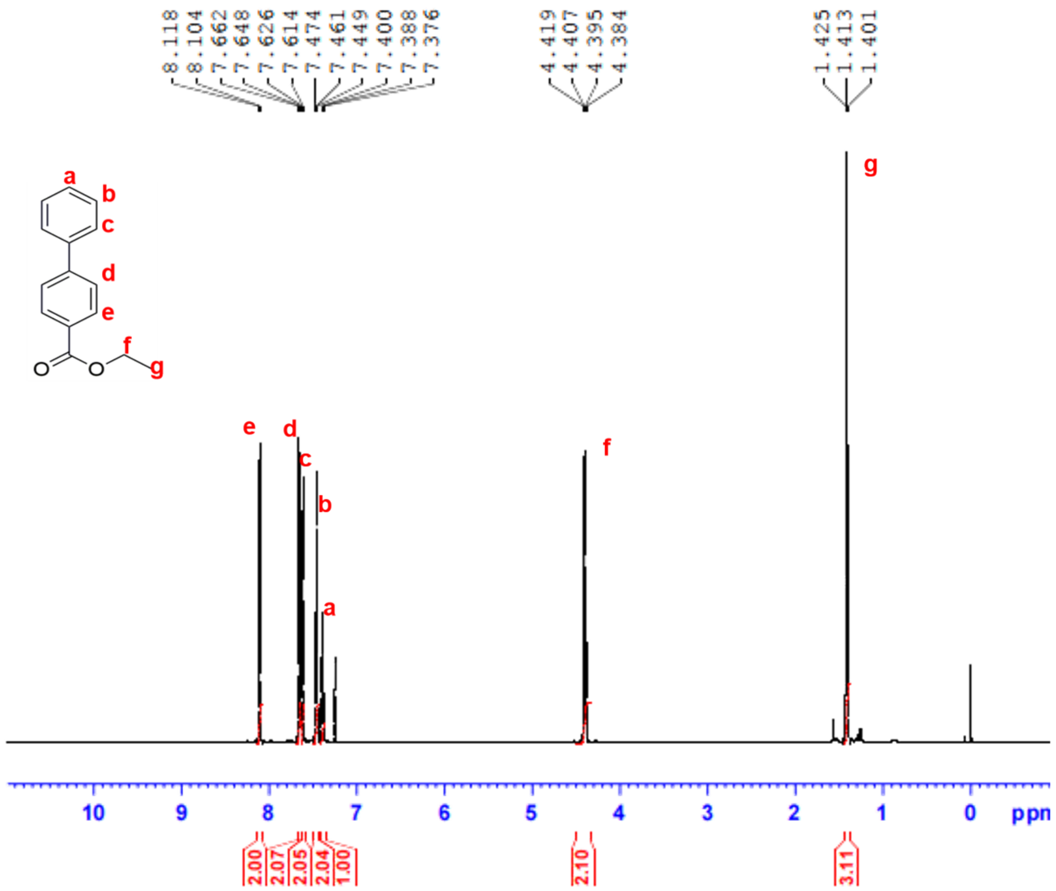


Scheme S5. Synthesis of diethyl 3',4'-bis(4-(ethoxycarbonyl)phenyl)-5',6'-bis(4-ethylphenyl)-[1,1':2',1''-terphenyl]-4,4''-dicarboxylate compound with carbon(IV) oxide (1:2) (**M5**).

Hexabromobenzene (4.00 g, 7.25 mmol), 4-methylphenylboronic acid pinacol ester (10.44 g, 47.87 mmol, 6.6 eq.), and potassium carbonate (12.09 g, 87.04 mmol, 12.00 eq.) were dissolved in 50 mL of a mixed solvent of 1,4-dioxane and DI water (v/v, 5/1). After the reactant mixture was bubbled with nitrogen for 20 min, 5% tetrakis(triphenylphosphine) palladium (0) (0.42 g, 0.36 mmol, 0.05 eq.) was quickly added and heated in a nitrogen atmosphere to reflux at 90 °C for 120 h. The reaction mixture was cooled to room temperature and filtrated. The residue was extracted with dichloromethane, washed with water, and dried with anhydrous magnesium sulfate. A colorless crystal ***a*** (3.87 g) was obtained with a yield of 86% after recrystallization from dichloromethane, and dried in a vacuum oven at 60 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 6.65 (q, 24H), 2.10 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 140.28, 138.00, 134.00, 131.29, 127.16, 21.05.

a (2.0 g, 3.23 mmol), concentrated HNO_3 (3 mL), and water (12 mL) were placed in a 40-mL autoclave and heated to 180 °C for 24 h. The resulting suspension was filtered to give a yellow crude product. Recrystallization from methanol afforded ***b*** (2.33 g, yielded 90%) as a yellow powder.

b (2.00 g, 2.51 mmol) was dissolved in $SOCl_2$ (20 mL, > 4. 40 mmol) and a drop of anhydrous DMF, the mixture was heated to reflux for ca. 24 h. Excess $SOCl_2$ was removed by atmospheric distillation to give a yellow solid. After cooling to 0 °C under an ice bath, the solid was dissolved in 20 mL anhydrous $CHCl_3$ and 4 mL ethyl alcohol, and then 5 mL trimethylamine diluted with 5 mL $CHCl_3$ was added dropwise. The mixture was heated to 40 °C for 24 h, washed with saturated NaCl aqueous solution, and the organic layer was dried with anhydrous $MgSO_4$. A pale yellow crystal **M5** (1.05 g) was obtained with a yield of 43% after purification by silica gel chromatography column with petroleum ether/ethyl acetate (v/v, 5/1) as the eluent. M. p.: > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.56 (d, J = 7.8 Hz, 12H), 6.89 (d, J = 7.8 Hz, 12H), 4.26 (q, 12H), 1.32 (t, J = 7.2 Hz, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 166.19, 144.00, 139.78, 130.94, 128.41, 128.21, 60.86, 14.16. HRMS (ESI) ($CHCl_3$, positive mode): m/z for $C_{60}H_{54}NaO_{12}$ $[M+Na]^+$: calculated: 989.3481, found: 989.3507.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4.407
4.395
4.384
1.425
1.413
1.401
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f
g
O
O
e
d
c
b
a
f
g
10
9
8
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2.05
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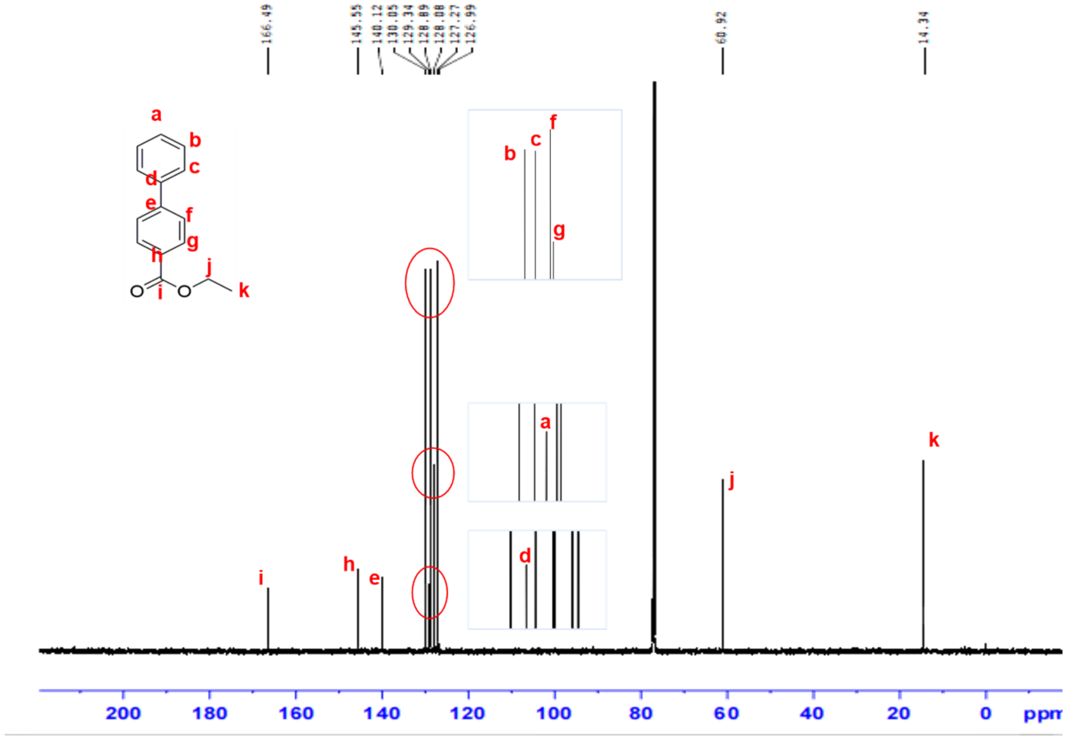
2.10
3.11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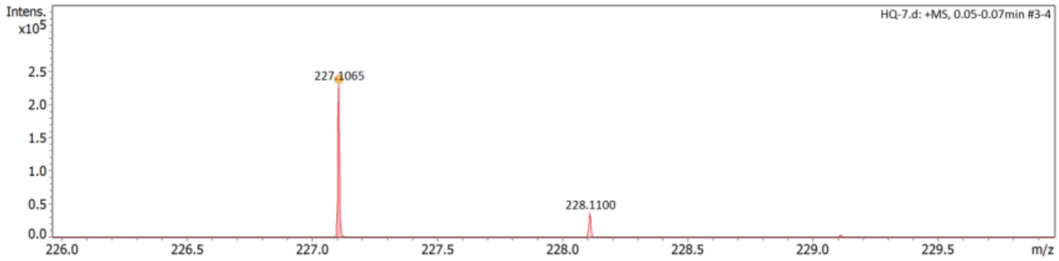

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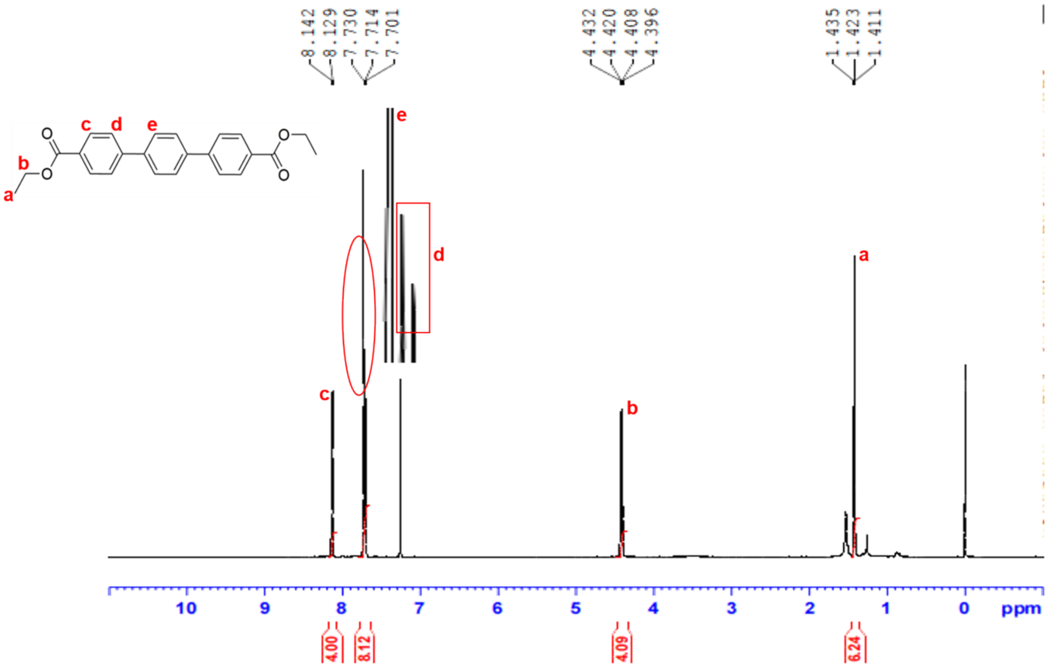
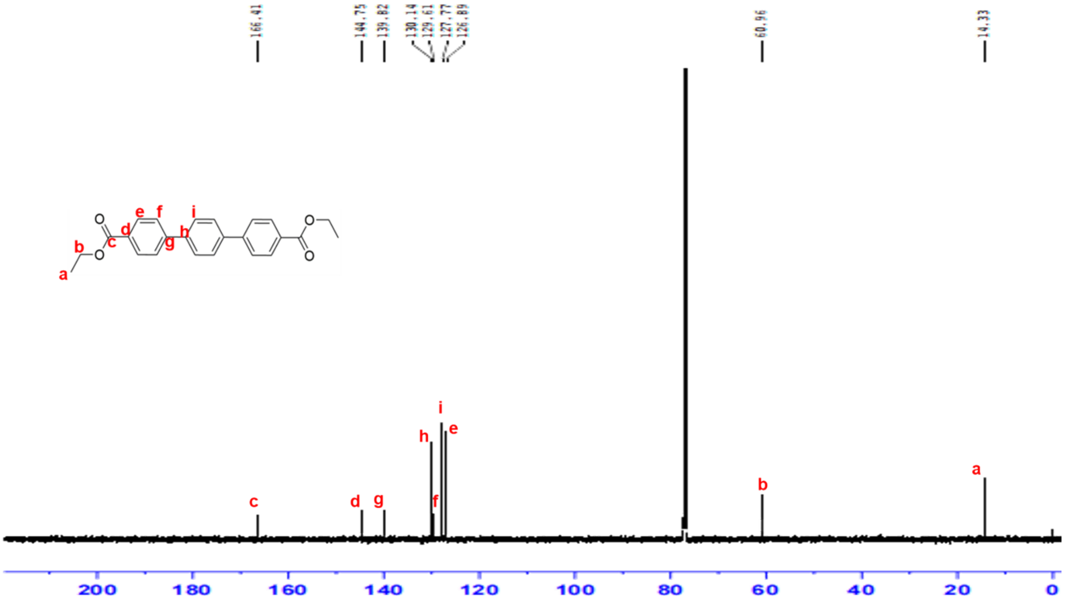
Fig. S1 ^{1}H NMR, ^{13}C NMR, and HRMS spectra of **M1**.





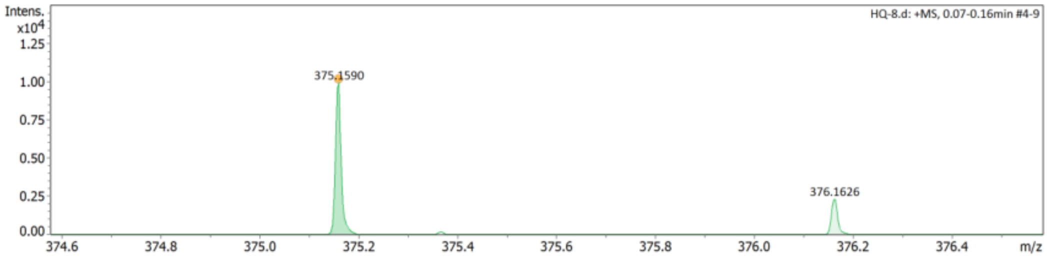


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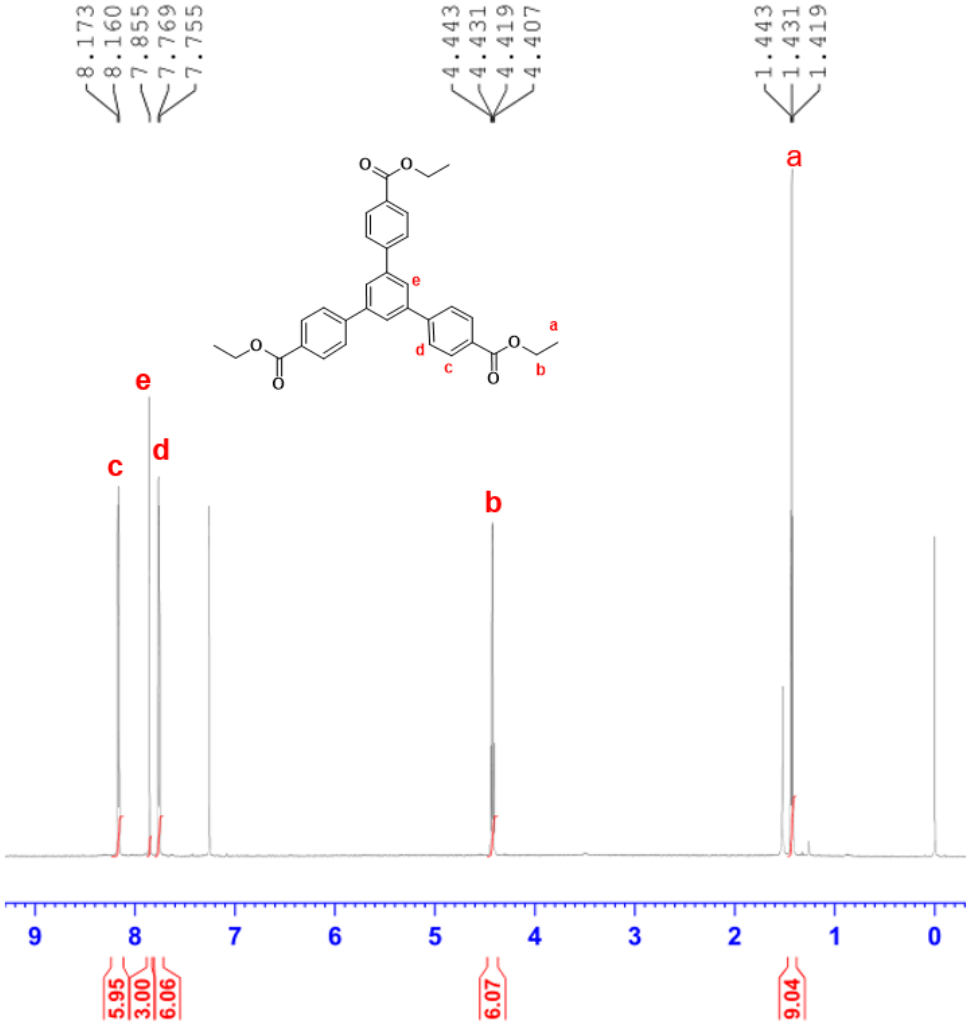
Fig. S2 ^{1}H NMR, ^{13}C NMR, and HRMS spectra of **M2**.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1.419
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b
c
d
e
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8
7
6
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4
3
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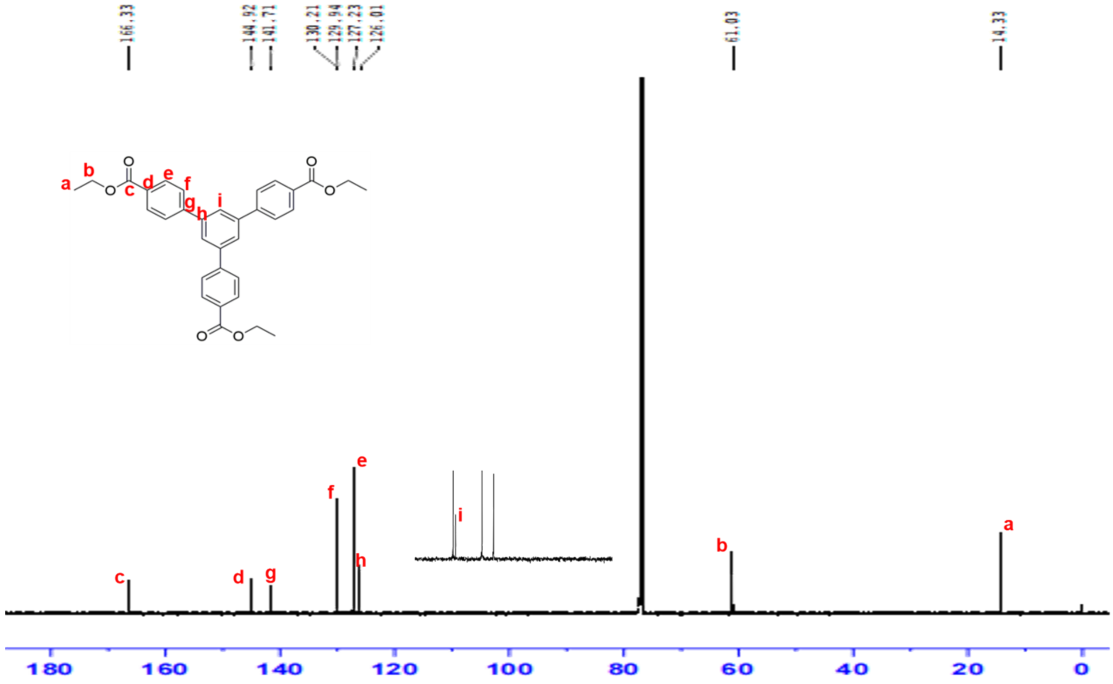
3.00
6.06
6.07
9.04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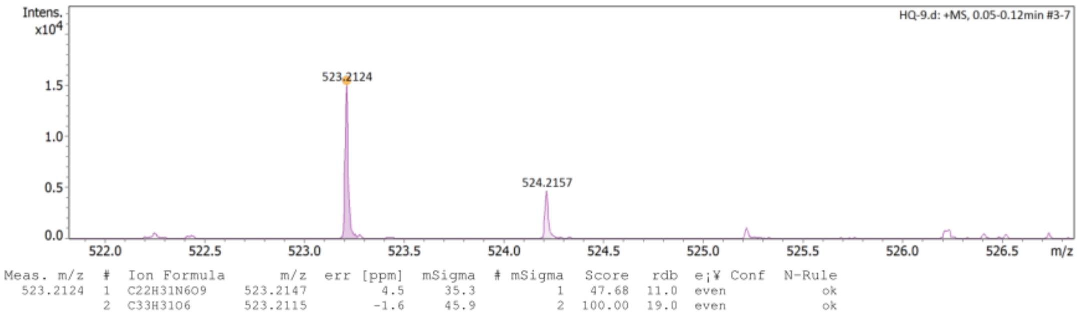

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            2  C33H31O6       523.2115       -1.6    45.9         2  100.00  19.0  even         ok
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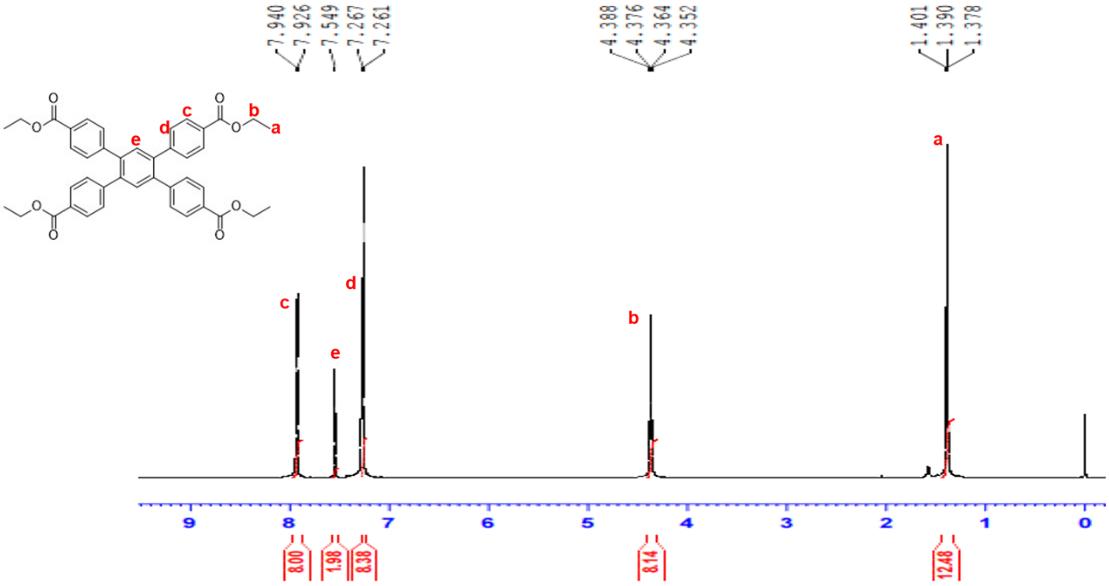
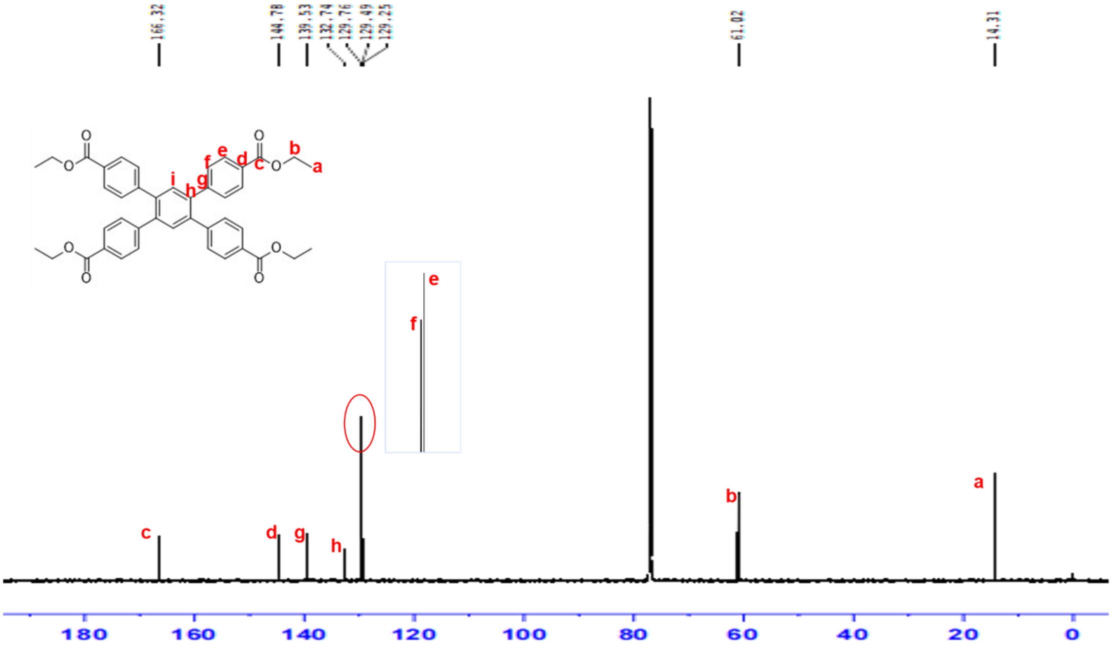
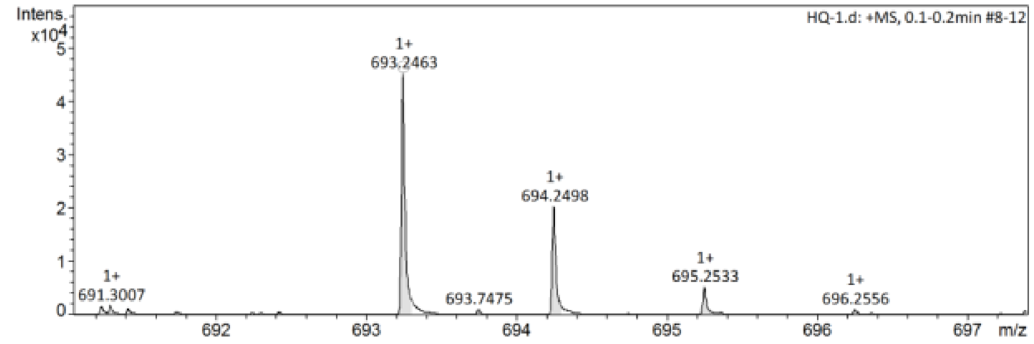
Fig. S3 ^{1}H NMR, ^{13}C NMR, and HRMS spectra of **M3**.

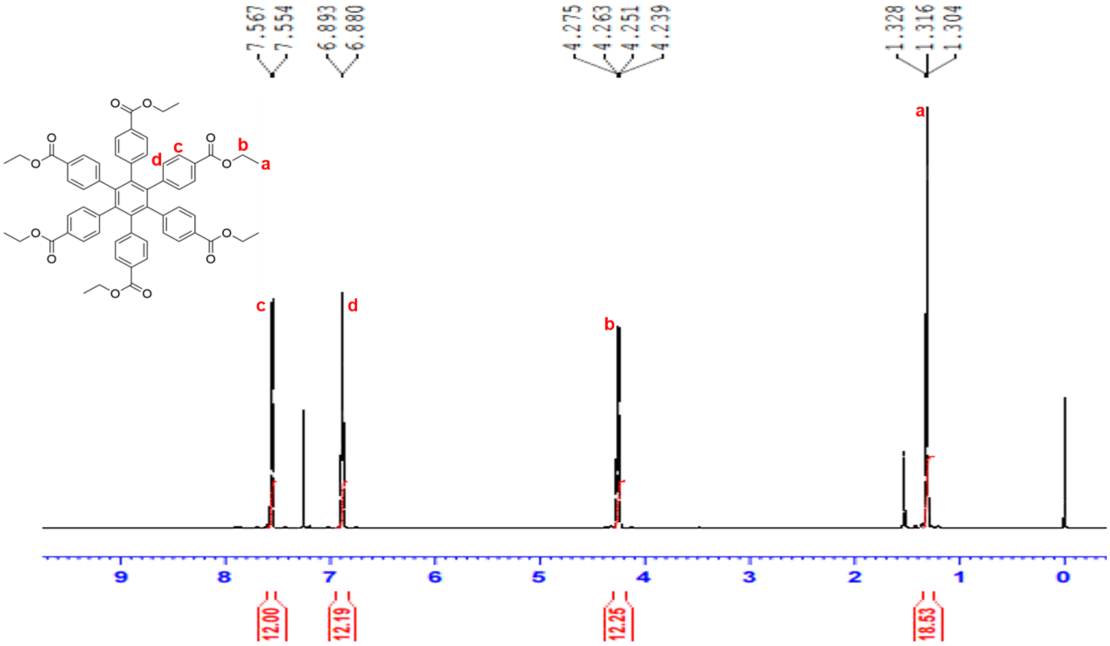


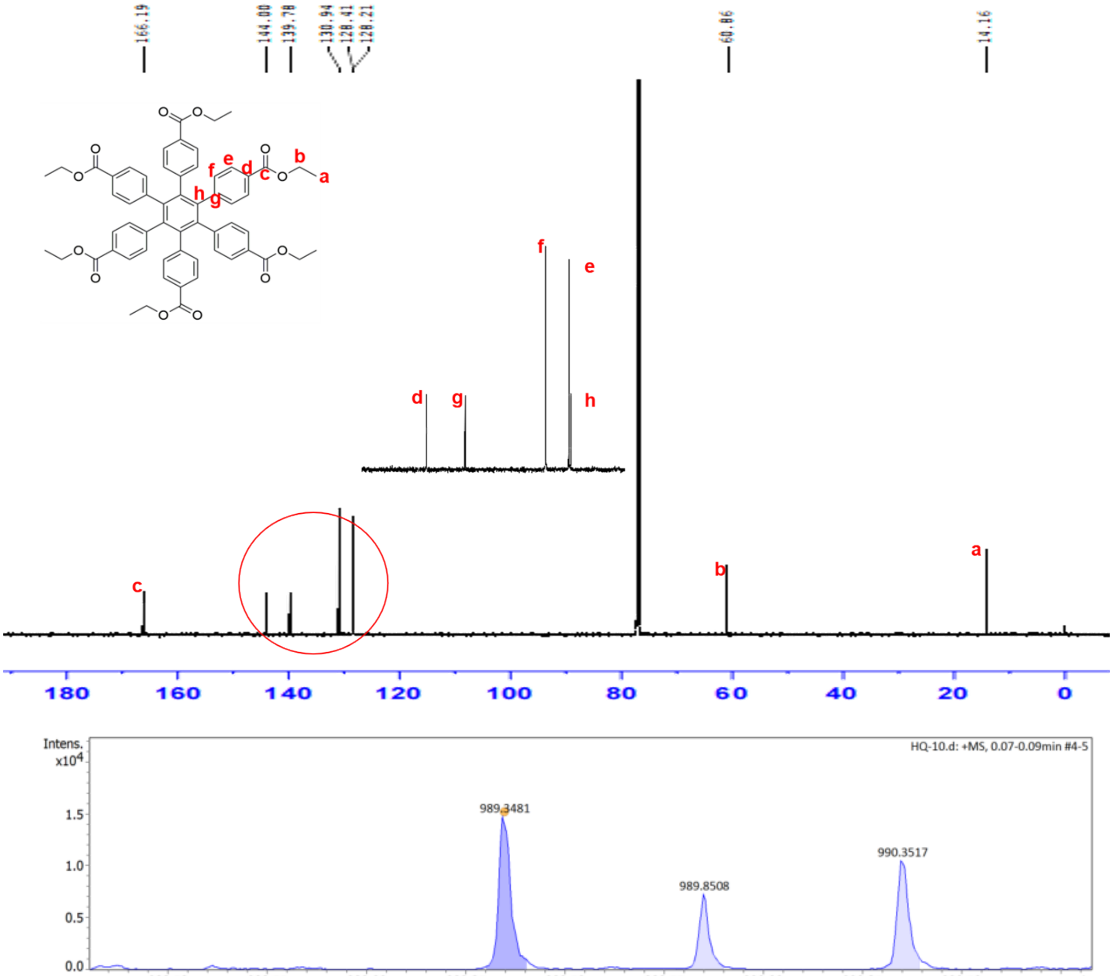




Meas. m/z	#	Ion Formula	Sum Formula	m/z	Adduct	err [ppm]	z	mSigma	Score	rdb	N-Rule	e⁻ Conf
693.2463	1	C42H38NaO8	C42H38O8	693.2459	M+Na	-0.6	1+	7.6	100.00	24.0	ok	even

Fig. S4 ^{1}H NMR, ^{13}C NMR, and HRMS spectra of **M4**.





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           2  C55H54N2NaO14 989.3467       -1.4    51.4         2  100.00  30.0  even          ok
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Fig. S5 ^{1}H NMR, ^{13}C NMR, and HRMS spectra of **M5**.

S2. Absorbance spectra of M1–M5 in NMP

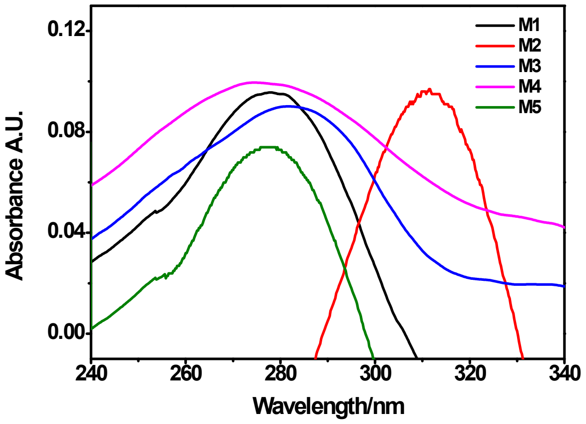


Fig. S6 Absorbance spectra of **M1**–**M5** in NMP (10^{-5} M).

S3. Torsion angles of M1–M5 obtained by DFT calculation

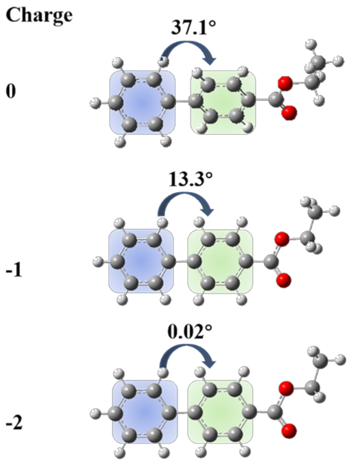


Fig. S7 Torsion angles of **M1** at different reductive states by DFT calculation.

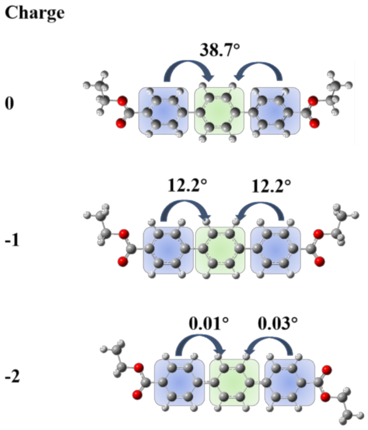


Fig. S8 Torsion angles of **M2** at different reductive states by DFT calculation.

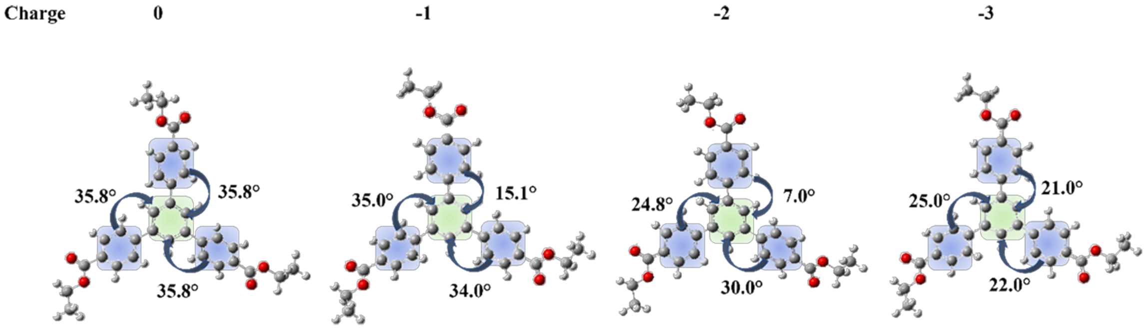


Fig. S9 Torsion angles of **M3** at different reductive states by DFT calculation.

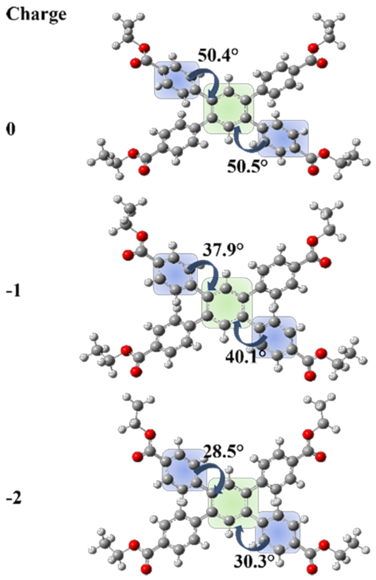


Fig. S10 Torsion angles of **M4** at different reductive states by DFT calculation.

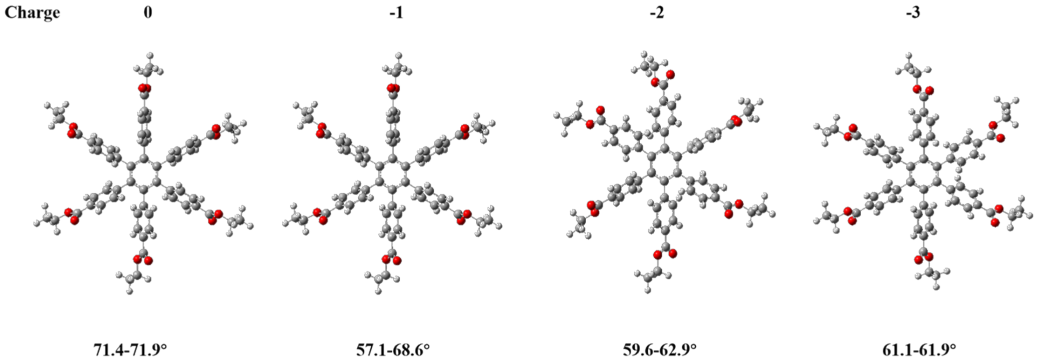


Fig. S11 Torsion angles of **M5** at different reductive states by DFT calculation.

S4. Cyclic voltammetry curves

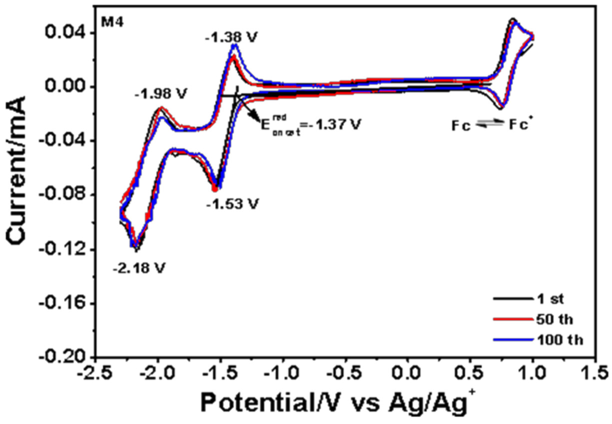


Fig. S12 Cyclic voltammetry curves of **M4** in anhydrous DMF under a nitrogen atmosphere at a scanning rate of 100 mV/s.

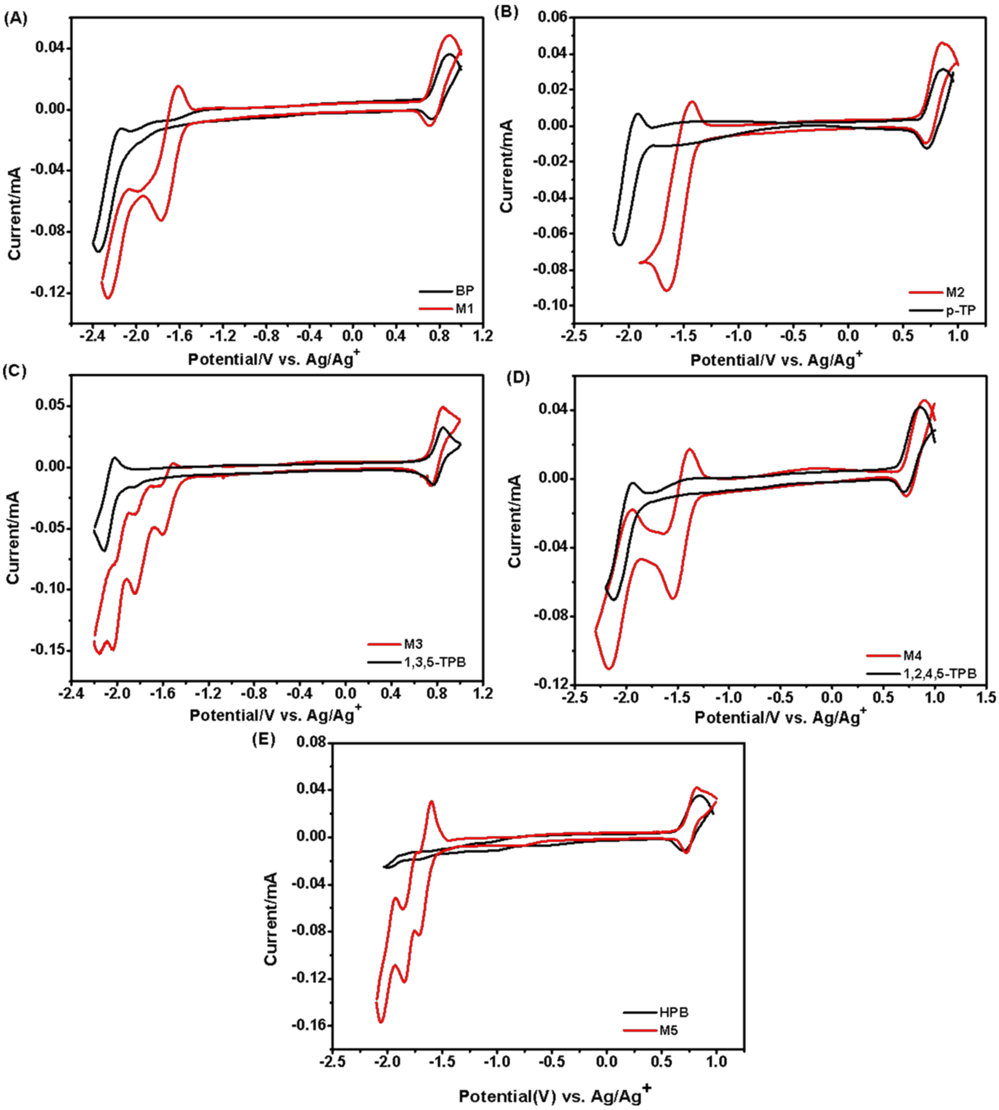


Fig. S13 Cyclic voltammetry curves of **M1** and Biphenyl (A), **M2** and p-Terphenyl (B), **M3** and 1,3,5-TPB (C), **M4** and 1,2,4,5-TPB (D), and **M5** and HPB (E) in anhydrous DMF under a nitrogen atmosphere at a scanning rate of 100 mV/s.

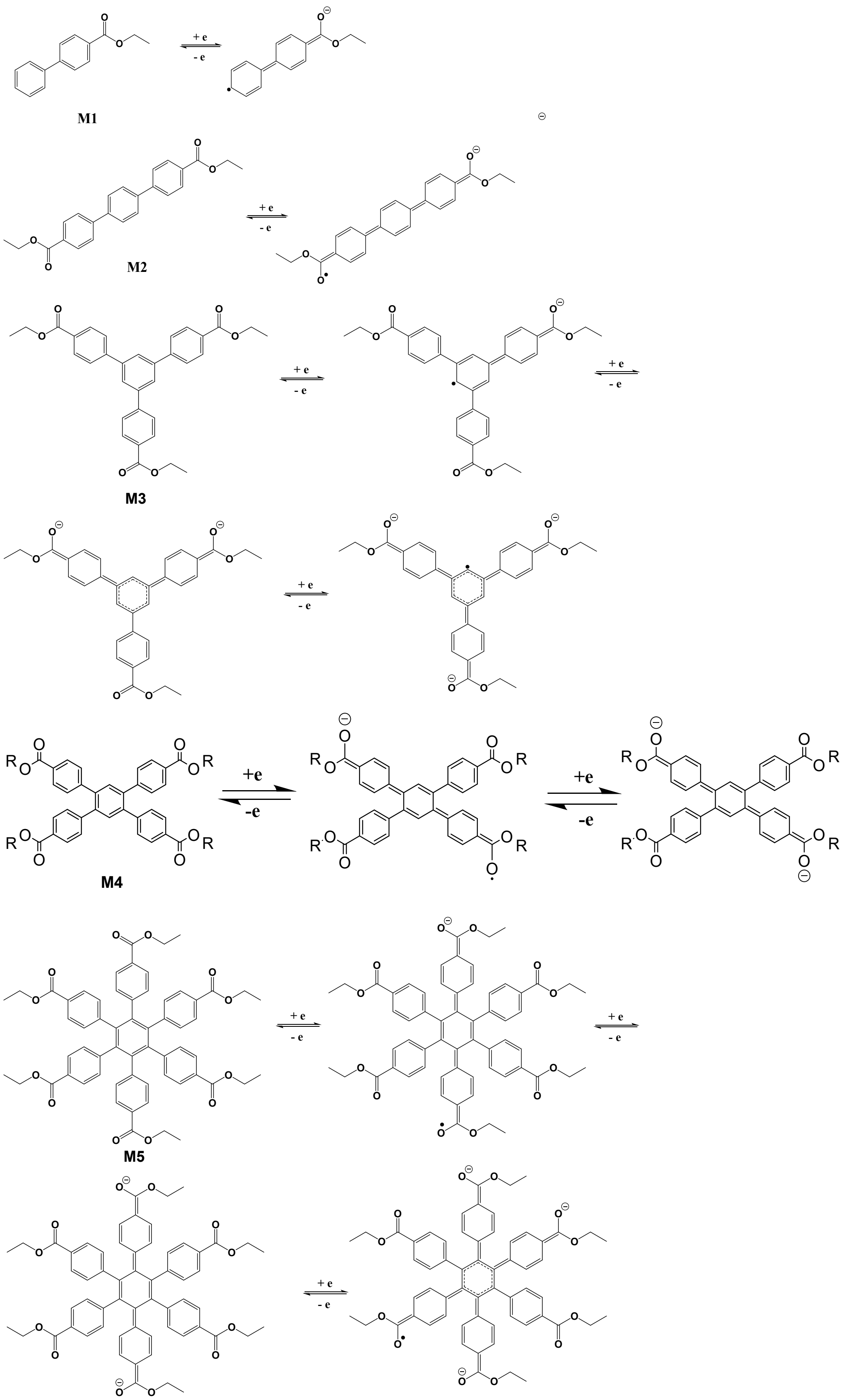


Fig. S14 Redox states of **M1–M5** in electrolyte solution.

S5. UV-Vis spectra of the ECDs based on polyphenyl nuclei

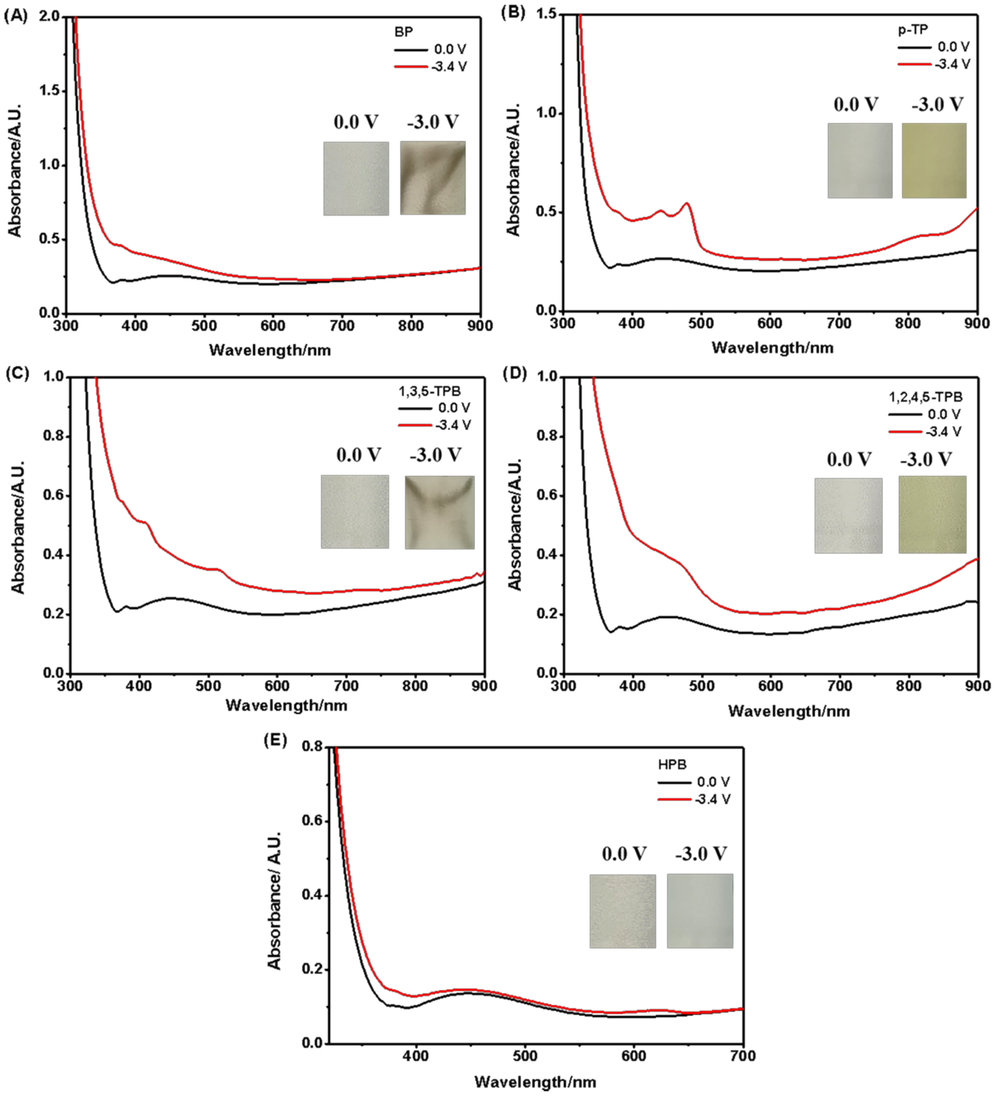


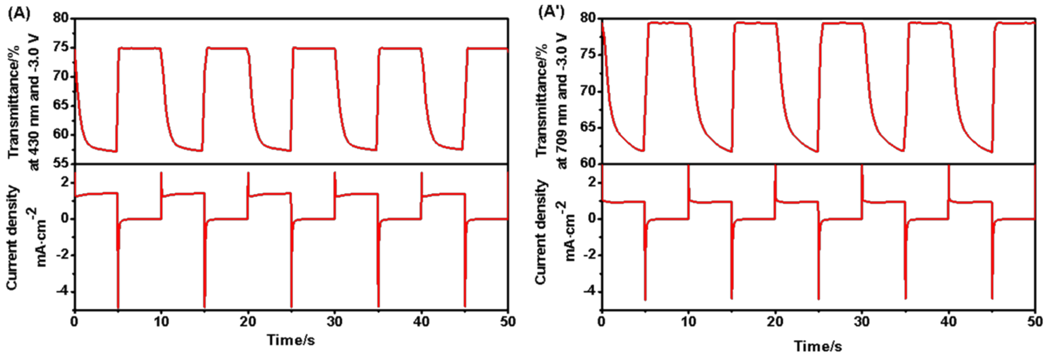
Fig. S15 UV-vis absorption spectra of ECDs based on Biphenyl (A), p-Terphenyl (B), 1,3,5-TPB (C), 1,2,4,5-TPB (D), and HPB (E) at 0.0 V and -3.4 V. Insets: Photographs of bleached and colored states of the ECDs under applied DC voltages of 0.0 and -3.0 V, respectively.

S6. The CIE chrominance coordinates of ECDs based on M1–M5

Table S1 CIE chromaticity values of electrochromic devices based on M1–M5 in bleached (0.0 V) and colored (-3.0 V) states.

Compound	Applied Voltage (V)	
	0.0 V	-3.0 V
M1	● L*a*b* : 54.5 -5.9 -8.6	● L*a*b* : 50.2 -19.1 -3.1
M2	● L*a*b* : 54.1 -5.4 -10.1	● L*a*b* : 45.5 12.3 -8.8
M3	● L*a*b* : 53.8 -5.1 -10.4	● L*a*b* : 47.2 -14.6 -6.8
M4	● L*a*b* : 58.2 -5.4 -6.8	● L*a*b* : 49.3 7.5 0.4
M5	● L*a*b* : 54.7 -5.5 -9.2	● L*a*b* : 46.5 -7.6 -7.1

S7. Chronoamperometry curves and the corresponding in-situ transmittance curves



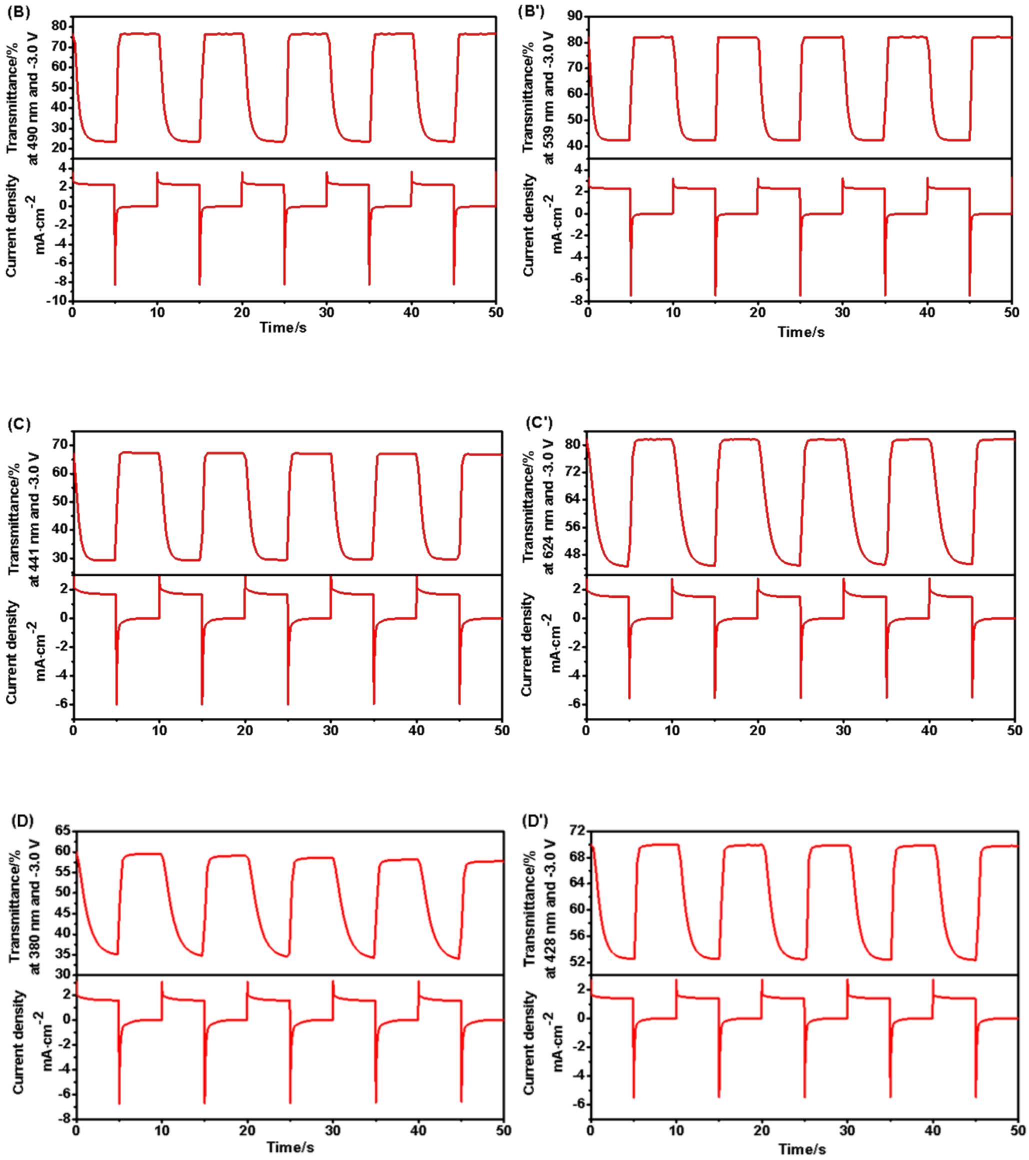


Fig. S16 Chronoamperometry curve and the corresponding in-situ transmittance curve of the ECDs based on compounds **M1** (A, at 430 nm; A', at 709 nm), **M2** (B, at 490 nm; B', at 539 nm), **M3** (C, at 441 nm; C', at 624 nm), and **M5** (D, at 380 nm; D', at 442 nm) between -3.0 and 0.0 V.

S8. Response time of the ECDs based on M1–M3 and M5

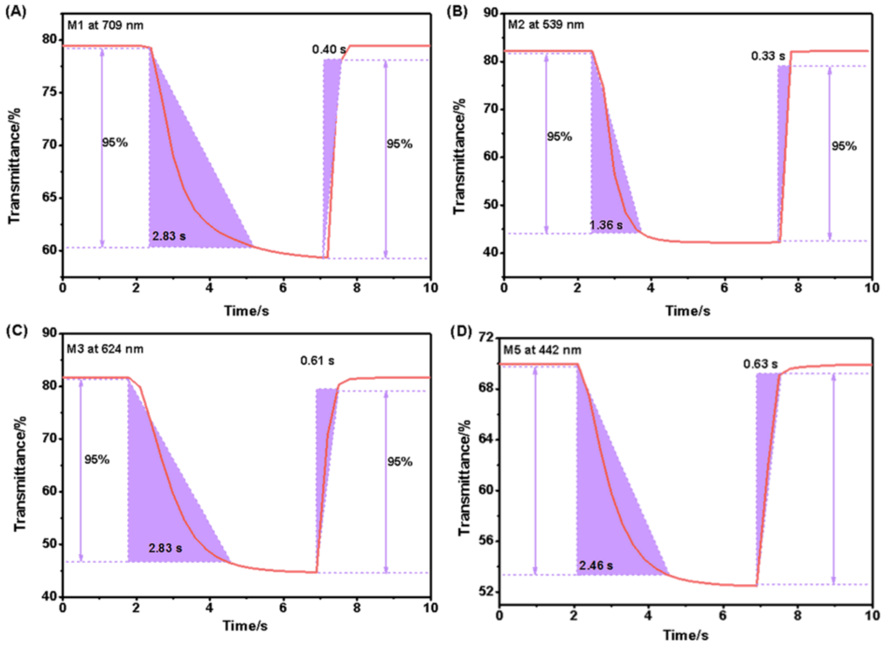


Fig. S17 Response times of the ECDs based on **M1** (A, at 709 nm), **M2** (B, at 539 nm), **M3** (C, at 624 nm), and **M5** (D, at 442 nm) between -3.0 V and 0.0 V.

S9. Spectral behavior of M1 in different solvents

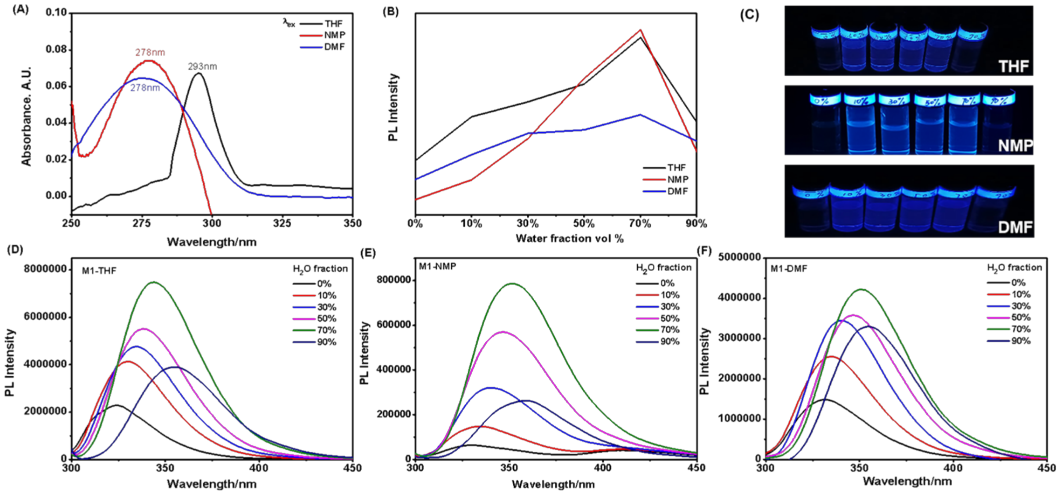


Fig. S18 (A) Absorbance spectra of M1. (B) Changes of PL Intensity of M1 versus water fraction in different solvent. (C) The photographs were taken under illumination of a 265 nm UV lamp. (D) PL spectra of M1 in THF/water mixtures with different water fractions. (E) PL spectra of M1 in NMP/water mixtures with different water fractions. (F) PL spectra of M1 in DMF/water mixtures with different water fractions.