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1,8-Dioxapyrene-Based Electrofluorochromic Supramolecular Polymers

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Supporting Information

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1. Materials and methods

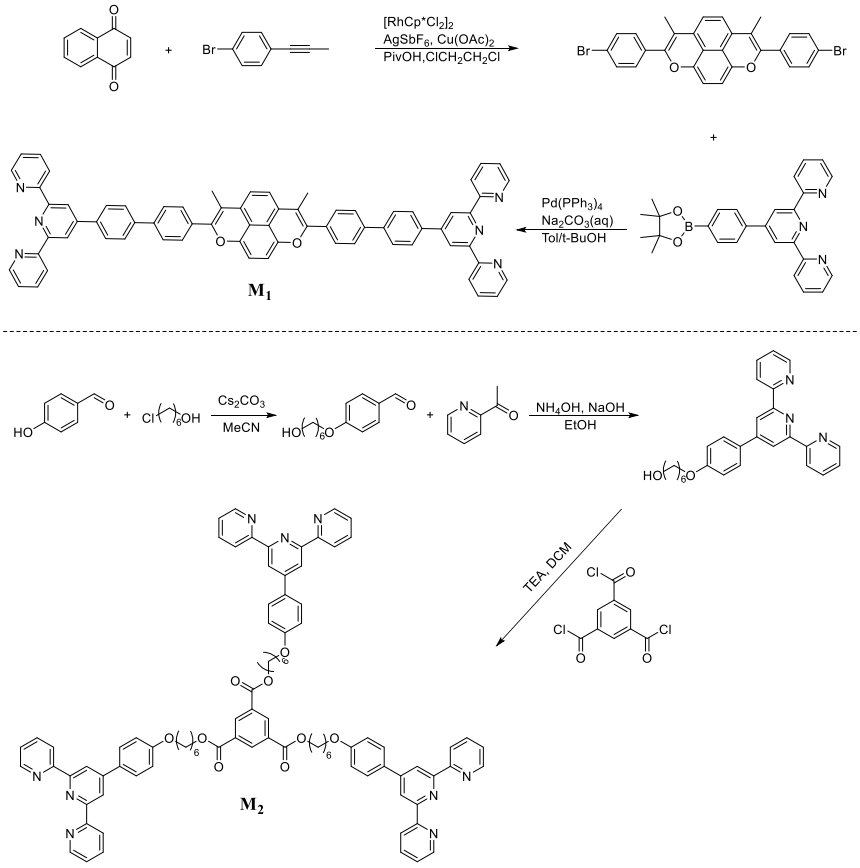
Alkyne, $Cu(OAc)_2$ and 1-dodecanethiol were purchased form Aladdin Reagents, China. Bis(triphenylphosphine)palladium(II) chloride, 4-iodoaniline, ethynyltrimethylsilane, and 1-bromododecane were purchased form TCI, Japan. EDC·HCl, 4-dimethylaminopyridine (DMAP), $[RhCp^*Cl_2]_2$ was purchased form J&K Scientific Ltd, China. 1,4-naphthoquinone, Tetrabutyl ammonium hexafluorophosphate, *p*-toluenesulfonyl chloride (TsCl) and TBAF (1M in THF) were purchased form Adamas, China. $AgSbF_6$ was purchased form Macklin and purified by washing with acetic acid and methanol before use. Other chemical reagents were purchased from Inno-Chem, China. Inorganic salts and organic solvents were purchased from Tianjin Kermel Chemical Reagents Development Center. Organic solvents were dried with 4 Å grade molecular sieves before use. All agents were used as received unless special statement.

^{1}H NMR and ^{13}C NMR spectra in solution were obtained from Bruker Avance 400 instruments. Electrospray Ionization Mass Spectrometry were obtained using a micro TOF-Q II 10280 (Varian Inc., USA) with suitable solvent. Ultraviolet visible (UV-vis) spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded with a Hitachi F-4600 FL Spectrophotometer. The time-resolved fluorescence lifetime experiments were performed with an Edinburgh FLS980 transient steady-state fluorescence spectrometer. Transmission electron microscopy (TEM) measurements were recorded on H-600 (Hitachi, Japan) with the acceleration voltage of 75 kV. Scanning electron microscopy (SEM) images were performed on a JEOL 6390LV instrument. Dynamic light scattering (DLS) experiments were conducted on a Malvern Instrument.

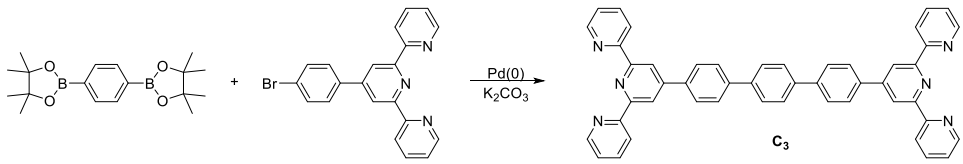
The electrofluorochromic behaviors of the samples in $CHCl_3/CH_3CN$ (1 : 1, *v/v*) were carried out with a potentiostat with a platinum disk electrode as working electrode and as counter electrode, and an Ag/AgCl electrode as the reference at room temperature. Bu_4NPF_6 was used as the supporting electrolyte.

Preparation of the liquid electrofluorochromic device: the colorful cartoon pattern was painted on a paper by using three different emission colors of EFSPs as anti-counterfeiting inks. Then, the liquid electrofluorochromic device was fabricated by encapsulating the pattern into Bu_4NPF_6 conductive solution (0.1 M in CH_3CN) and sandwiching between two indium-tin oxide (ITO) anode. The applied voltage is supplied by a potentiostat.

*2. Synthetic routes to monomers **M₁**, **M₂** and **M₃***



Scheme S1. Synthetic routes to monomers **M₁** and **M₂**.



Scheme S2. Synthetic route to monomer **M₃**

2.1 Synthesis of 2,7-bis(4-bromophenyl)-3,6-dimethylisochromeno[7,8,1-def]chromene.

1,4-naphthoquinone (158 mg, 1.0 mmol), alkyne (582 mg, 3.0 mmol), $[RhCp^*Cl_2]_2$ (30 mg, 5 mol%), $AgSbF_6$ (68 mg, 20 mol%), $Cu(OAc)_2$ (200 mg, 1.0 mmol), pivalic acid and DCE (5 mL) were stirred under an N_2 atmosphere at 130 °C for 24 hours. After the reaction, the mixture solution was subsequently diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with dichloromethane for three times. The combined organic phases were evaporated, and the residue was purified by flash column chromatography (petroleum ether/CH_2Cl_2, 10 : 1 *v*/*v* as the

eluent) to afford compound 2,7-bis(4-bromophenyl)-3,6-dimethylisochromeno[7,8,1-def]chromene as an orange solid (261 mg, 48 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.5 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 6.39 (d, J = 7.6 Hz, 4H), 1.77 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.90, 146.63, 133.46, 131.36, 130.54, 129.18, 124.06, 115.17, 109.42, 108.27, 13.18. ESI-MS (m/z): $[M + H]^+$, 545.6338.

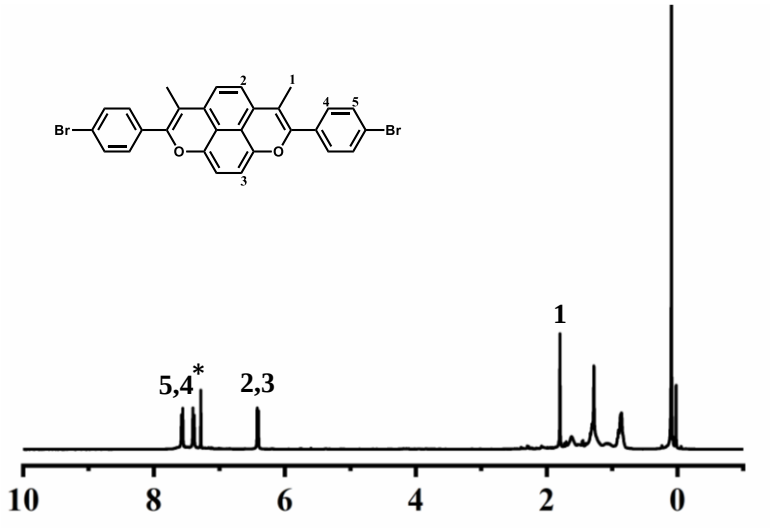


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of compound 2,7-bis(4-bromophenyl)-3,6-dimethylisochromeno[7,8,1-def]chromene.

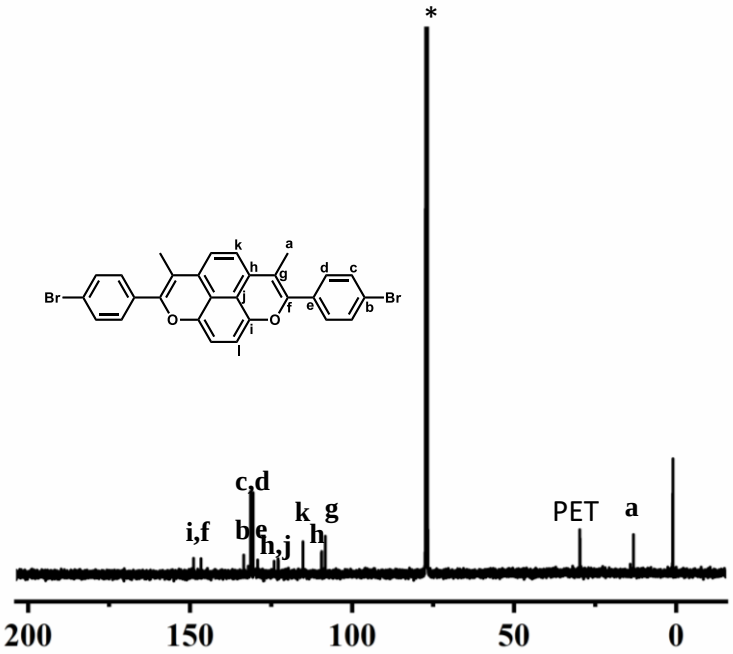


Figure S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of compound 2,7-bis(4-bromophenyl)-3,6-dimethylisochromeno[7,8,1-def]chromene.

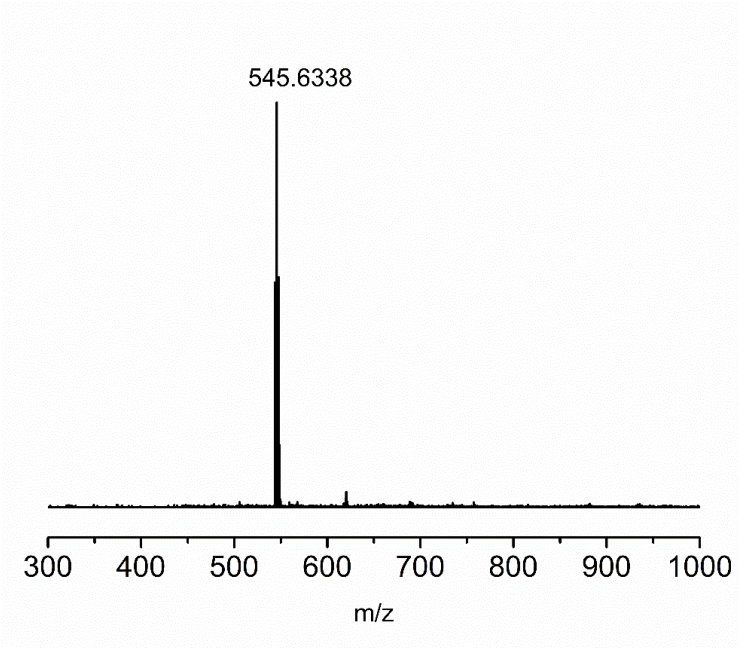


Figure S3. ESI-MS spectrum of 2,7-bis(4-bromophenyl)-3,6-dimethylisochromeno[7,8,1-def]chromene.

2.2 Synthesis of monomer ***M₁***

2,7-bis(4-bromophenyl)-3,6-dimethylisochromeno[7,8,1-def]chromene (545 mg, 1.0 mmol), 4'-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-2,2':6',2''-terpyridine (957 mg, 2.2 mmol), and $Pd(PPh_3)_4$ (120 mg, 0.1 mmol) were added into a Schlenck tube and degassed with N_2. Aqueous Na_2CO_3 (4 M, 20 mL) and toluene (50 mL) were degassed using N_2 and then injected into the Schlenck tube. After stirring in the dark at 110 °C for 72 hours, the reaction mixture was evaporated to remove the solvent, and the residue was extracted with H_2O/CH_2Cl_2 for three times. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed with a rotary evaporator. The residue was purified by flash column chromatography (CH_2Cl_2/THF, 15 : 1 *v*/*v* as the eluent) to afford compound **M₁** as a red solid (626 mg, 62 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 4H), 8.75 (d, *J* = 4.3 Hz, 4H), 8.70 (d, *J* = 7.8 Hz, 4H), 8.04 (d, *J* = 8.2 Hz, 4H), 7.90 (t, *J* = 7.8 Hz, 4H), 7.79 (d, *J* = 7.9 Hz, 4H), 7.75 (d, *J* = 8.2 Hz, 4H), 7.64 (d, *J* = 7.7 Hz, 4H), 7.39–7.35 (m, 4H), 6.45 (d, *J* = 14.9 Hz, 4H), 1.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.24, 156.00, 149.15,136.96, 136.94, 134.95, 132.17, 132.58, 132.10, 132.00, 131.98, 131.89, 129.96, 129.43, 129.35, 128.68, 128.60,

128.56, 128.48, 127.84, 127.58, 127.39, 126.80, 123.90, 121.43, 118.71, 109.30, 108.28, 13.34. ESI-MS (*m/z*): $[M + H]^+$, 1002.3411.

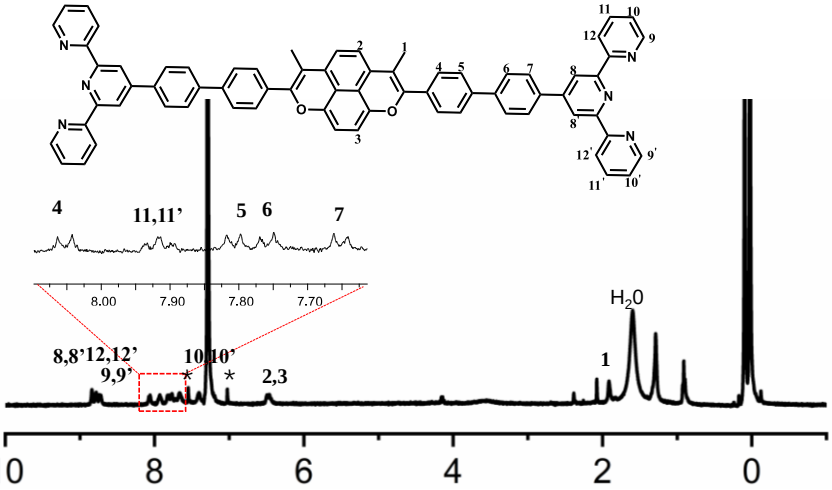


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of monomer **M₁**.

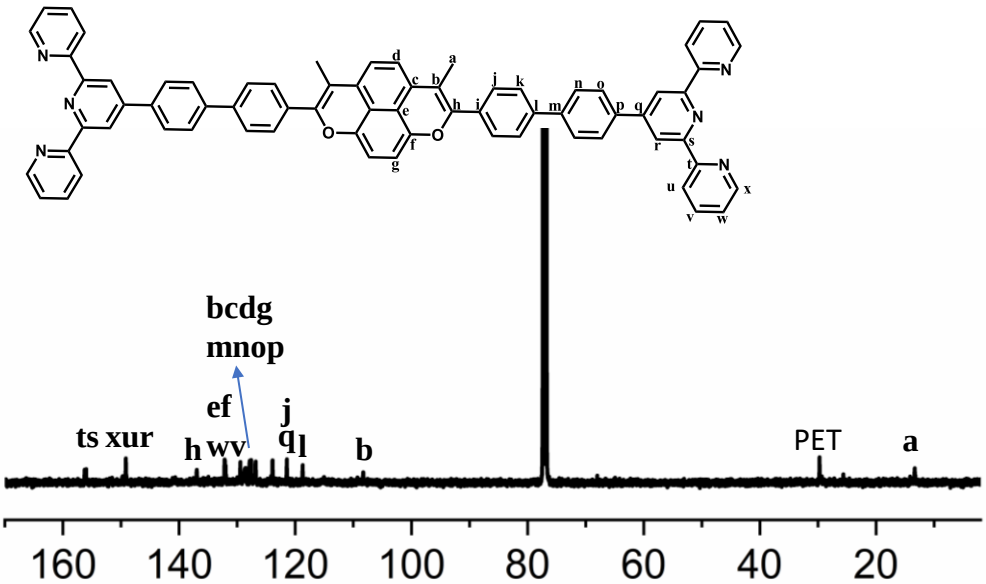


Figure S5. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of monomer **M₁**.

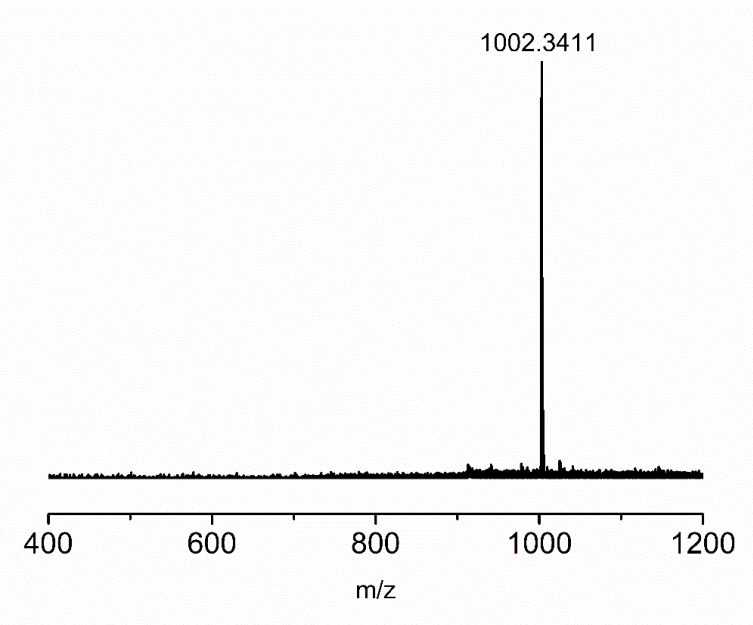


Figure S6. ESI-MS spectrum of monomer **M1**.

2.3 Synthesis of compound 4-((6-hydroxyhexyl)oxy)benzaldehyde

4-hydroxybenzaldehyde (1.22 g, 10 mmol), Cs_2CO_3 (4.25 g, 30 mmol), 6-Chloro-1-hexanol (1.63 g, 12 mmol) and CH_3CN (30 mL) were stirred at 85 °C for 12 hours. After that, the reaction mixture was evaporated to remove the solvent, the residue was extracted with H_2O/CH_2Cl_2 for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed with a rotary evaporator. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 10 : 1, *v/v* as the eluent) to give compound 4-((6-hydroxyhexyl)oxy)benzaldehyde as a white solid (1.96 g, 88 %).[S1] ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.76 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H),3.98 (t, J = 6.5 Hz, 2H), 3.60 (t, J = 6.6 Hz, 2H), 2.52 (s, 1H), 1.81–1.73 (m, 2H), 1.60–1.52 (m, 2H), 1.49–1.36 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ 191.02, 164.25, 132.03, 129.64, 114.74, 68.27, 62.58,32.56, 28.99, 25.78, 25.51.

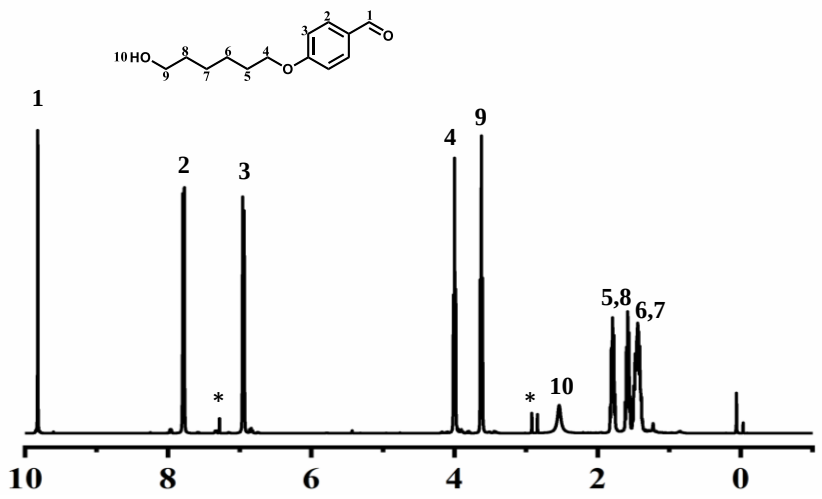


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of 4-((6-hydroxyhexyl)oxy)benzaldehyde.

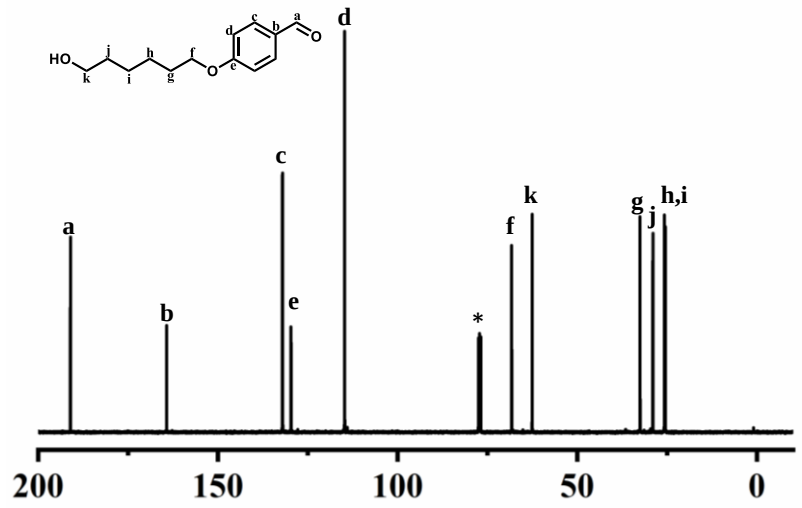


Figure S8. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of 4-((6-hydroxyhexyl)oxy)benzaldehyde.

2.4 Synthesis of compound 6-(4-([2,2':6',2''-terpyridin]-4'-yl)phenoxy)hexan-1-ol

4-((6-hydroxyhexyl)oxy)benzaldehyde (2.22 g, 10 mmol), 2-Acetylpyridine (4.25 g, 30 mmol), NaOH (1.63 g, 12 mmol) and EtOH (30 mL) were stirred at room temperature for 2 hours, and then ammonia water was added into the mixture. After refluxing for 12 hours, the reaction mixture was cooled to ambient temperature, the precipitate was filtered and recrystallized from ethanol to afford 6-(4-([2,2':6',2''-terpyridin]-4'-yl)phenoxy)hexan-1-ol as white crystals (3.41 g, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77–8.72 (m, 2H), 8.71 (s, 2H), 8.67 (d, J = 8.0 Hz, 2H), 7.88 (m, 2H), 7.35 (m, 2H), 7.05–6.98 (m, 2H), 4.04 (t, J = 6.5 Hz, 2H), 3.68 (t, J = 6.5 Hz, 2H), 1.87–1.82 (m, 2H), 1.66–1.60 (m, 2H), 1.57–1.44 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ 160.08, 156.38, 155.80, 149.78, 149.08, 136.90, 130.46, 128.49, 123.79, 121.42, 118.24, 114.85, 67.96, 62.80, 32.70, 29.24, 25.91, 25.60. ESI-MS (*m/z*): $[M + H]^+$, 426.9248.

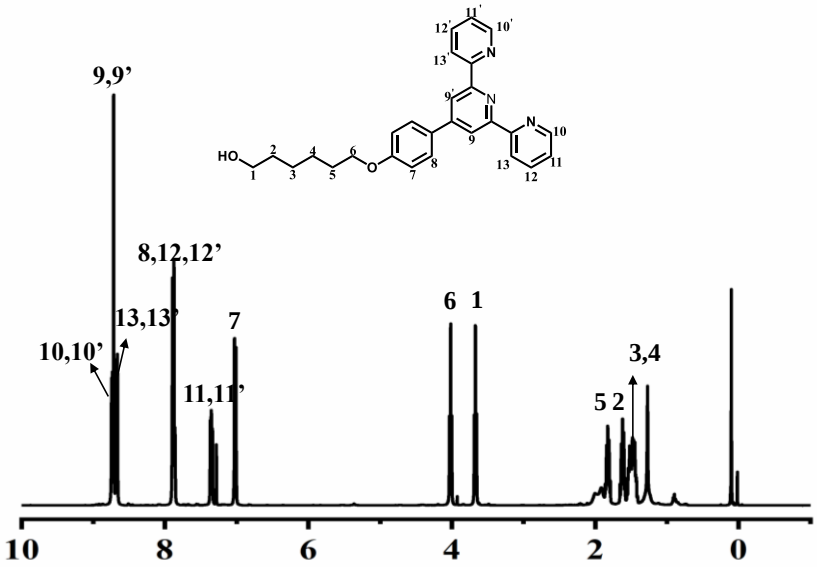


Figure S9. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of 6-(4-([2,2':6',2"-terpyridin]-4'-yl)phenoxy)hexan-1-ol.

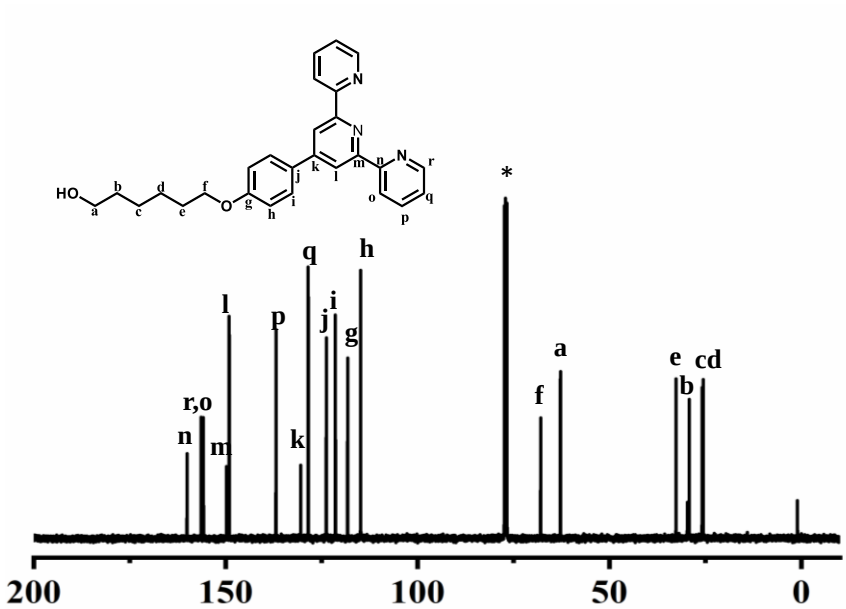


Figure S10. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of 6-(4-([2,2':6',2"-terpyridin]-4'-yl)phenoxy)hexan-1-ol.

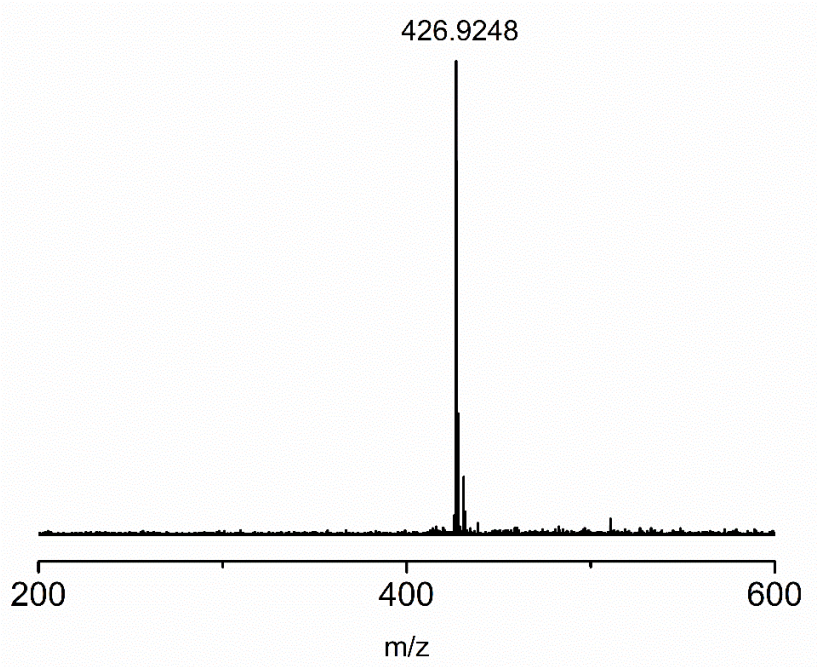


Figure S11. ESI-MS spectrum of 6-(4-([2,2':6',2"-terpyridin]-4'-yl)phenoxy)hexan-1-ol.

2.5 Synthesis of monomer ***M₂***

6-(4-([2,2':6',2"-terpyridin]-4'-yl)phenoxy)hexan-1-ol (2.13 g, 5 mmol) was stirred in triethylamine (4.25 g, 30 mmol) and DCM (30 mL). Trimesoylchloride was added dropwise to the reaction mixture over 2 hours. After stirring at room temperature for 12 hours, the reaction mixture was evaporated to remove the solvent, and the residue was extracted with H_2O/CH_2Cl_2 for three times. The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed with a rotary evaporator. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 10 : 1 *v*/*v* as the eluent) to give **M₂** as white solids (5.15 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.72 (d, J = 4.6 Hz, 2H), 8.68 (s, 2H), 8.65 (d, J = 7.9 Hz, 2H), 7.90–7.80 (m, 4H), 7.33 (dd, J = 6.9, 5.1 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 4.40 (t, J = 6.6 Hz, 2H), 4.02 (t, J = 6.3 Hz, 2H), 1.92–1.79 (m, 4H), 1.58–1.51 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.11, 160.04, 156.31, 155.72, 149.73, 149.04, 136.92, 134.49, 131.47, 130.43, 128.48, 123.78, 121.42, 118.23, 114.83, 67.85, 65.74, 29.17, 28.61, 25.83. ESI-MS (*m/z*): $[M + H]^+$, 1432.8523.

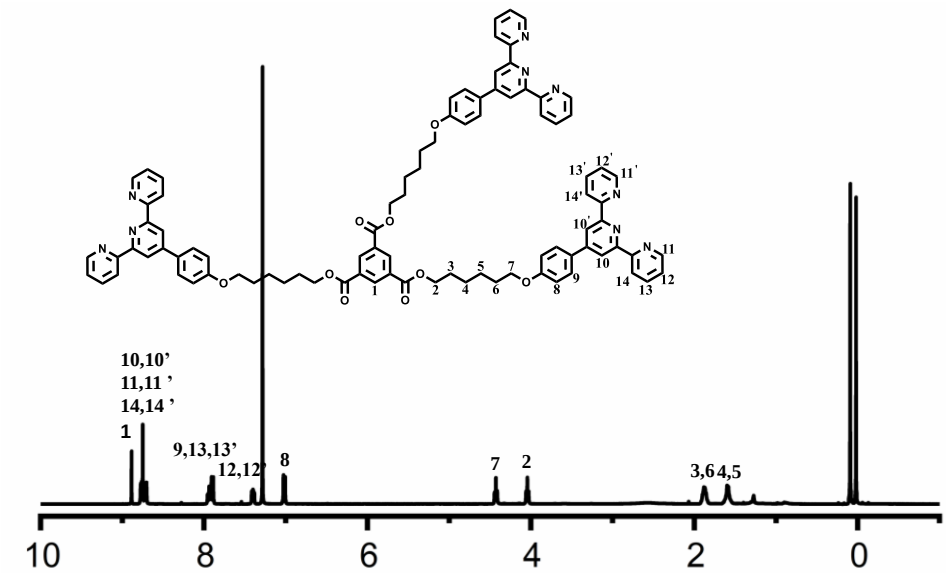


Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of monomer **M₂**.

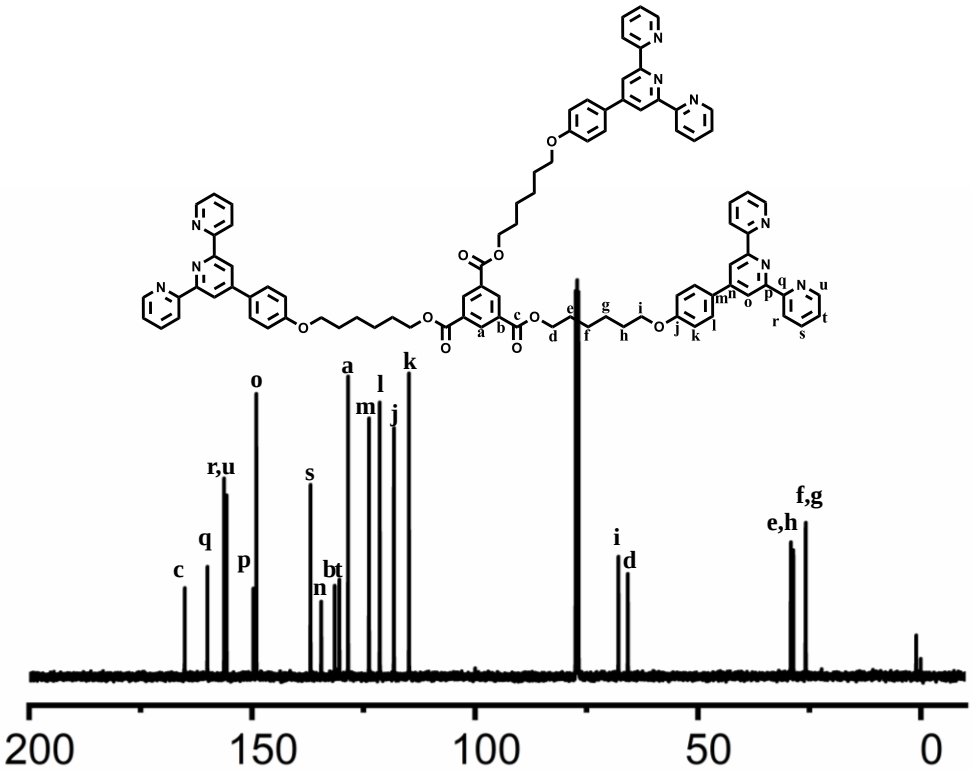


Figure S13. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of monomer **M₂**.

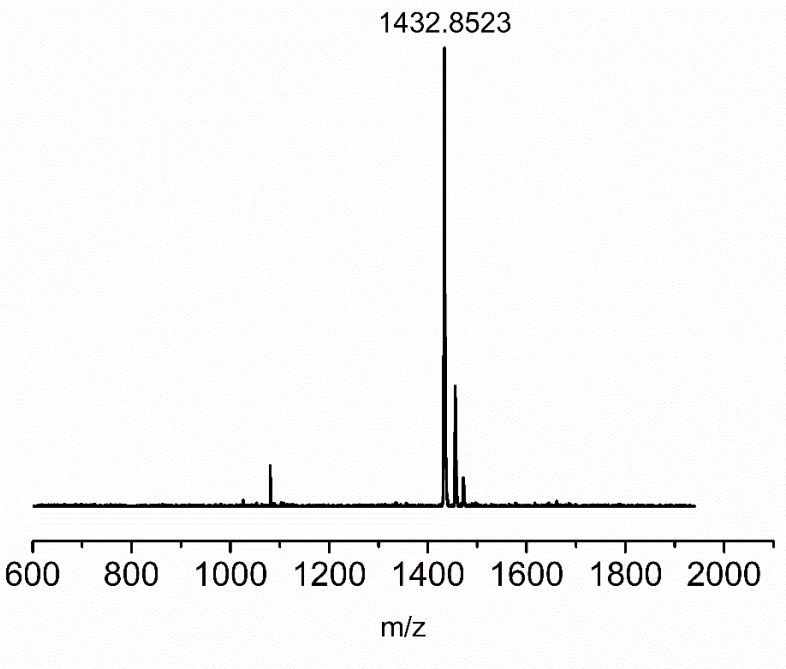


Figure S14. ESI-MS spectrum of monomer $\mathbf{M_2}$.

2.6 Synthesis of monomer $\boldsymbol{M_3}$

1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (4.26 g, 11 mmol) and 4'-(4-bromophenyl)-2,2':6',2"-terpyridine (1.65 g, 5 mmol) were dissolved in THF under N_2. K_2CO_3 (2.07 g, 15 mmol) in H_2O was added and degassed by freeze pump thaw cycle three times. Tetrakis(triphenylphosphine)palladium(0) (577 mg, 0.5 mmol) was then added and followed by freeze-pump-thaw cycle once more. The mixture was refluxed overnight. After cooling to room temperature, the mixture was pour into water and extracted with CH_2Cl_2 for three times. The combined organic extracts were dried over anhydrous Na_2SO_4, and then the solvent was removed, the resulting residue was recrystallized from methanol to give $\mathbf{M_3}$ as white solids (2.35 g, 68%)[S2] . ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 4H), 8.76 (d, J = 4.3 Hz, 4H), 8.70 (d, J = 8.0 Hz, 4H), 8.05 (d, J = 8.2 Hz, 4H), 7.90 (m, J = 7.8, 1.6 Hz, 4H), 7.83 (d, J = 8.3 Hz, 4H), 7.80 (d, J = 3.6 Hz, 4H), 7.38 (dd, J = 6.9, 5.2 Hz, 4H).

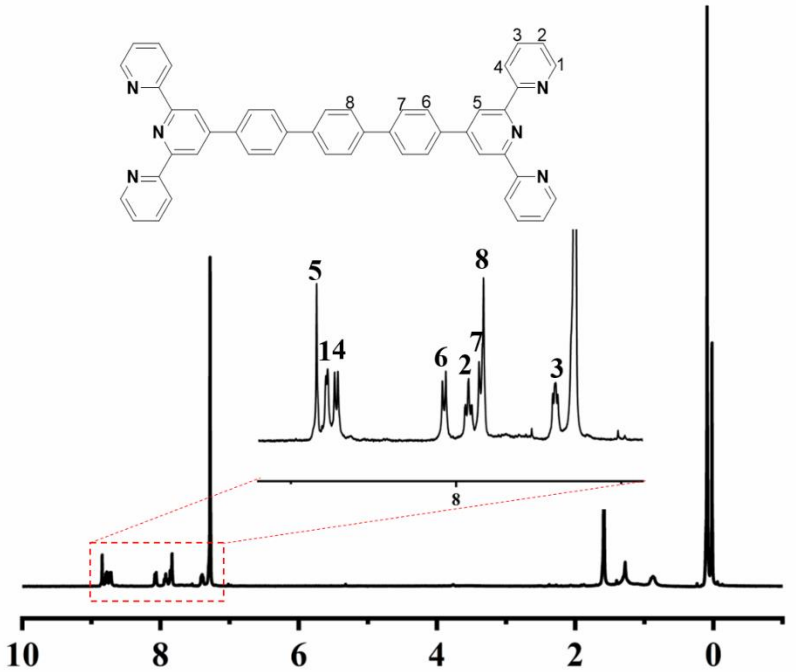


Figure S15. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of monomer $\mathbf{M_3}$.

3. Multicolor tunable emission of the EFSPs

Table S1. Optical Properties of the EFSPs with different molar ratio of $\mathbf{M_1}$ and $\mathbf{M_2}$

EFSPs	λ_{em} [nm][a]	Φ_F[b]
$\mathbf{M_1}$: $\mathbf{M_2}$ = 3 : 2	452	0.52
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 1	453	0.48
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 2	457	0.46
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 3	458	0.45
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 4	459	0.43
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 5	462	0.39
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 7	465	0.37
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 8	622	0.36
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 9	622	0.35
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 10	622	0.33
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 12	622	0.21
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 15	622	0.19
$\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 20	622	0.18

[a] λ_{em} = emission maximum, λ_{ex} = 340nm. [b] Φ_F = fluorescence quantum yield in dilute $CHCl_3$-CH_3CN (1/1, *v/v*) solution estimated by Rhodamine B (70% in ethanol). FSPs = fluorescent supramolecular polymers.

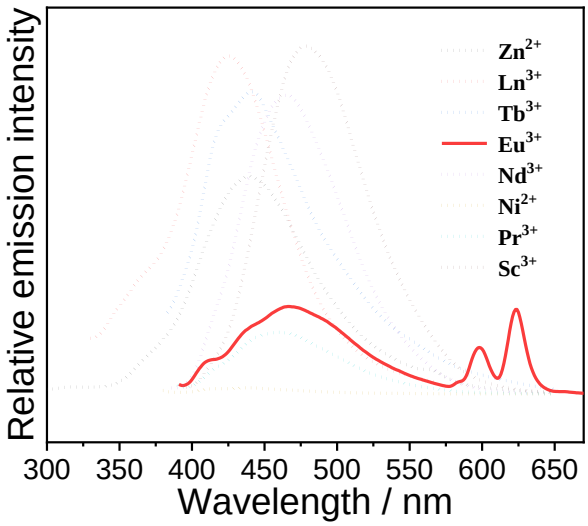


Figure S16. Fluorescence spectra of the EFSPs constructed by $\mathbf{M_1}$ and $\mathbf{M_2}$ ($\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 1) with different metal ions. The emission color of the FSPs based on metal-ligand coordination

interactions can be fine-tuned by introducing different metal ions. However, for the purpose of achieving white-light emission color EFSPs, the Zn^{2+}, Ln^{3+}, Tb^{3+}, Nd^{3+}, Ni^{2+}, Pr^{3+} and Sc^{3+} ions are all not suitable, because of the single emission band for the resulting FSPs. Interestingly, the EFSPs based on Eu^{3+} ions exhibit three distinct emission peaks at blue area (452nm) and red area (598nm, 622nm), which enables to achieve the multicolor tunable emission (from blue to red, and passes through white) by adjusting the molar ratio of $\mathbf{M_1}$ and $\mathbf{M_2}$.

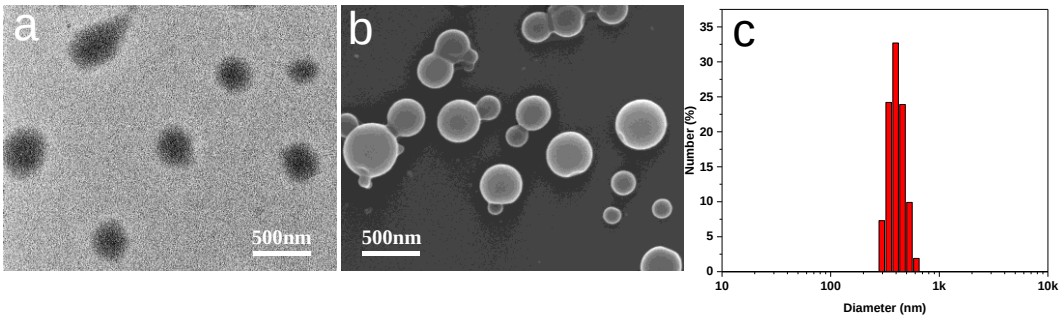


Figure S17. a) TEM, b) SEM and c) DLS measurements for the EFSPs ($\mathbf{M_1}$: $\mathbf{M_2}$ = 1 : 10).

4. Electrofluorochromic properties of the EFSPs

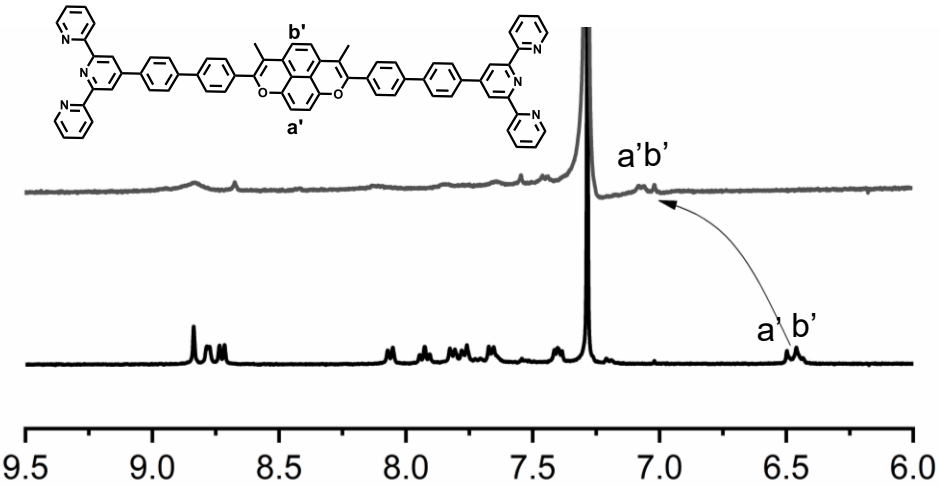


Figure S18. Partial ^{1}H NMR spectra (400 MHz, $CDCl_3$, 293 K) of $\mathbf{M_1}$ after applying a positive voltage of 1.5 V. When a 1.5 V voltage is applied to the solution of $\mathbf{M_1}$, the 1,8-dioxapyrene resonances ($H_{a'}$ 6.47 ppm, $H_{b'}$ 6.44 ppm) disappearance, together with the emergence of a new set of resonances in the downfield region ($H_{a'}$ 7.06 ppm, $H_{b'}$ 7.03 ppm). Such phenomena reveal the conversion from $\mathbf{M_1}$ to its electrochemical products.

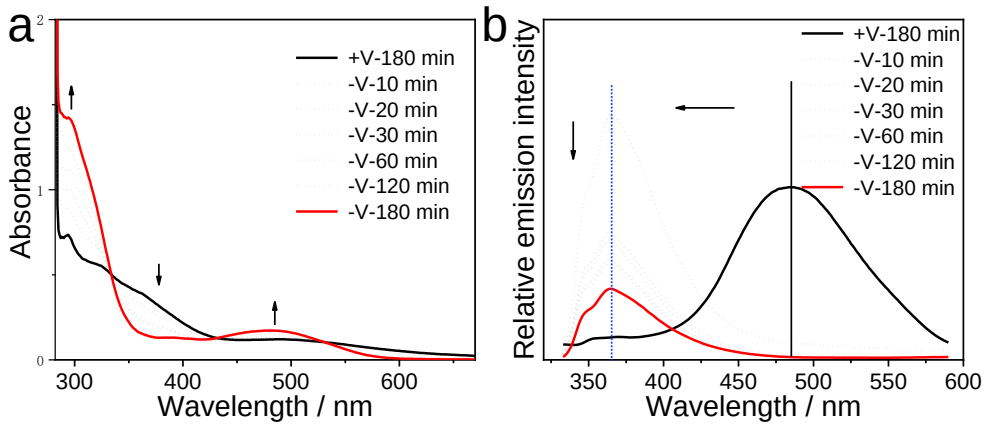


Figure S19. (a) UV−Vis and (b) fluorescence spectra variations of $\mathbf{M_1}$ (0.01 mM in $CHCl_3$/MeCN = 1 : 1 *v*/*v*) after positive voltage treatment and then upon continuously applying a negative voltage. When the solution of $\mathbf{M_1}$ is applying with negative voltage of −1.5 V, the UV−Vis and emission spectra are completely recovered, together with the emission color returns to being blue emission. The concentrations in (a) and (b) are 0.01M in $CHCl_3$/MeCN = 1 : 1, *v*/*v* with 0.1 M tetrabutyl ammonium hexafluorophosphate as electrolyte.

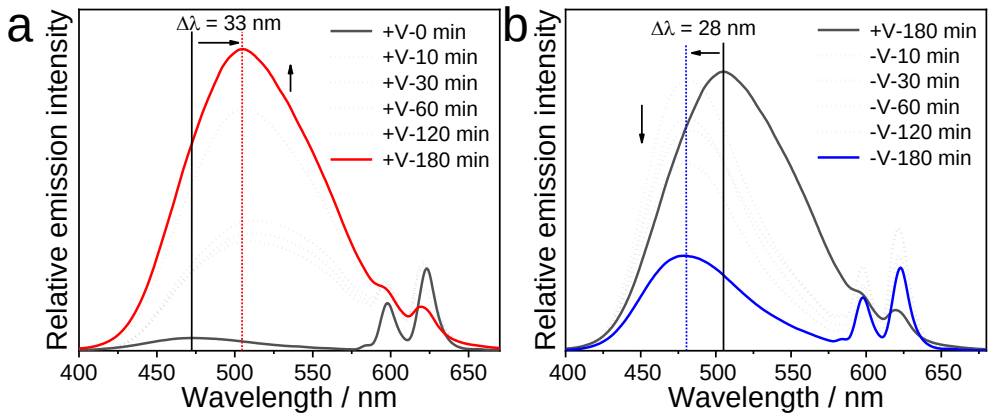


Figure S20. Fluorescence spectra variations of the EFSPs (**M_1** : **M_2** = 1 : 20 in $CHCl_3$/MeCN = 1 : 1 *v*/*v*) (a) upon continuously applying a positive voltage of +1.5 V, (b) and then a negative voltage of −1.5 V. When a positive voltage of +1.5V is incessantly applied to the solution of the red emission FSPs (**M_1** : **M_2** = 1:20), the emission band at 472nm gradually red-shifts to 505nm, together with enhanced intensity. During this process, the fluorescent color is gradually dominated by the band of 505 nm, which changes from red to green. Furthermore, when the positive voltage is converted to negative one, the emission band at 504nm blue-shifts to 481nm, and the intensity gradually decreases as the energization time is extended. The emission color of the solution varies from green to blue.

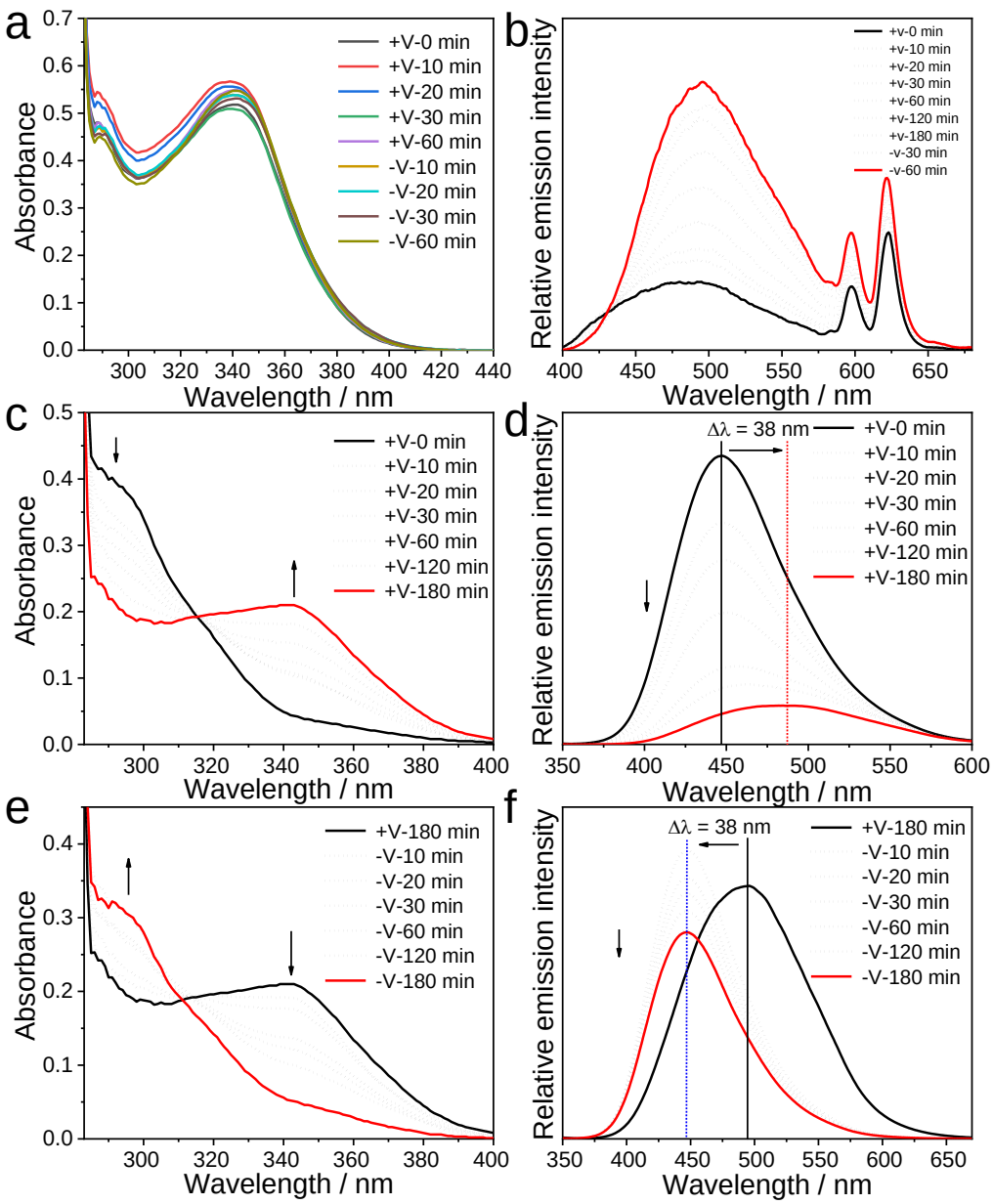


Figure S21. (a) UV−Vis and (b) fluorescence spectra variations of the EFSPs (**M₃** : **M₂** : Eu^{3+} = 1 : 20 : 31 in $CHCl_3$/MeCN = 1 : 1 *v*/*v*) upon continuously applying a positive voltage of +1.5 V. (c) UV−Vis and (d) fluorescence spectra variations of the EFSPs (**M₁** : **M₂** : Mg^{2+} = 1 : 20 : 31 in $CHCl_3$/MeCN = 1 : 1 *v*/*v*) upon continuously applying a positive voltage of +1.5 V. (e) UV−Vis and (f) fluorescence spectra variations of the EFSPs (**M₁** : **M₂** : Mg^{2+} = 1 : 20 : 31 in $CHCl_3$/MeCN = 1 : 1 *v*/*v*) after positive voltage treatment and then upon continuously applying a negative voltage of −1.5 V.

References

S1. Piñol, R., *Chemistry of Materials*, 2008, **20**, 6076.

S2. M. Higuchi, *Polym. J.*, 2010, **42**, 336.