Electronic Supplementary Information

High-contrast Reversible Multiple Color-tunable Solid Luminescent Ionic Polymers for Dynamic Multilevel Anti-counterfeiting

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Materials and Methods

General Information. All of the chemicals were obtained from commercial sources and used without further purification. The used chloromethyl polystyrene resin **P** (0.8-1.2 *mmol/g*) in this work have been commercially available from TCI (Shanghai) Development Co. Ltd. NMR measurements were carried out on a Bruker DMX500 spectrometer using tetramethylsilane (TMS) as an internal standard. TGA measurements were carried out with METTLER TOLEDO TGA/DSC1/1600HT. IR spectra were recorded in the range of 400-4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Avance X-ray powder diffractometer with Cu *K*α (1.5418 Å). Fluorescence spectra for the solid samples were recorded at room temperature on an Edinburgh Model FS5 instrument, and emission quantum yields were recorded on integrating sphere SC-30. The calibration of quantum yields for the powder samples is conducted with a matched integrating sphere. At first, the emission of the blank integrating sphere was measured, and then the emission of the integrating sphere containing the powdery samples was measured. Finally, the quantum yields could be obtained according

to the calibration. Luminescence lifetimes (τ) were examined using an Edinburgh Model FS5 phosphorimeter.

Syntheses of ligand and small molecule ionic compounds

2,6-di(naphthalen-2-yl)-4,4'-bipyridine (**L**): In a 250 mL round bottom flask, 1-(naphthalen-2-yl)ethan-1-one (3.60 g, 21.2 mmol), NH_3 (aqueous) (40 mL) and KOH (2.4 g, 42.8 mmol) were respectively added to a solution of 4-pyridinecarboxadehyde (1.14 g, 10.6 mmol) in EtOH (100 mL). The reaction mixture was stirred at room temperature for 48 h. The resultant precipitate was collected by filtration and washed with methanol many times and then recrystallized by ethanol. A pure white solid was obtained. ^{1}H NMR: (400 MHz, $CDCl_3$) δ: 8.87 (2 H, d, *J* 4.0), 8.74 (2 H, s), 8.46 (2 H, d, *J* 4.0), 8.12 (2 H, s), 8.10~8.04 (4 H, m), 8.10~8.04 (4 H, m), 8.00~7.94 (2 H, m), 7.78 (2 H, d, *J* 4.0), 7.65~7.55 (4 H, m), 7.31 (2 H, s). ^{13}C NMR: (400 MHz, DMSO-D6) δ: 157.4, 151.0, 147.6, 145.4, 136.4, 134.0, 133.7, 129.3, 128.9, 128.2, 127.4, 127.1, 125.3, 122.4, 117.6. HRMS (ESI): m/z Calcd. for [$C_{30}H_{20}N_2$, L]: 408.50; Found: 408.85. IR (KBr, cm^{-1}): 3054(m), 3018(m), 1586(s), 1532(s),1508(w), 1442(m), 1400(s), 1339(m), 1201(m), 1147(m), 913(s), 865(w), 816(m), 756(s), 636(s), 564 (m).

L-Cl: Benzyl chloride (0.084 g, 0.66 mmol) was added into a solution of **L** (0.25 g, 0.61 mmol) in CH_3CN (15 mL) and the reaction mixture was stirred at 100 °C under N_2 for 12 h. The resultant yellow precipitate was collected by filtration and washed with CH_3CN and DCM, giving the yellow product of **L-Cl** with the yield above 85%. ^{1}H NMR: (400 MHz, DMSO-D6) δ: 9.52 (2 H, d, *J* 6.8), 9.00 (4 H, m), 8.72 (2 H, s), 8.62 (2 H, m), 8.15 (4 H, m), 8.04 (2 H, m), 7.64 (6 H, m), 7.48 (3 H, m), 5.95 (2 H, s). ^{13}C NMR: (400 MHz, DMSO-D6) δ: 157.7, 153.9, 145.8, 144.1, 136.0, 135.2, 134.1, 133.6, 130.0, 129.8, 129.3, 129.0, 128.3, 127.7, 127.3, 127.1, 125.1, 118.3, 63.5. HRMS (ESI): m/z Calcd. for [$C_{37}H_{27}N_2$, L]$^+$: 499.64; Found: 498.85. IR (KBr, cm^{-1}): 3054(m), 3006(m), 2922(m), 1634(s), 1592(m),1544(s), 1406(s), 1237(m), 1201(m), 1153(m), 847(s), 822(s), 762(s), 738(s), 708(s), 630 (w).

L-PF$_6$: Excess NH_4PF_6 (100 mg) was added into a solution of **L-Cl** (150 mg) in CH_3OH (15 mL). The reaction mixture was stirred at room temperature for 12 h. The resultant yellow microcrystals with the yield of ~90% were collected by filtration and washed with CH_3OH. ^{1}H NMR: (400 MHz, DMSO-D6) δ: 9.53 (2 H, d, *J* 6.8), 9.03 (4 H, m), 8.73 (2 H, s), 8.63 (2 H, d, *J* 8.7), 8.16 (4 H, m), 8.05 (2 H, m), 7.64 (6 H, m), 7.48 (3 H, m), 5.93 (2 H, s). ^{13}C NMR: (400 MHz, DMSO-D6) δ: 157.7, 154.0, 145.7, 144.2, 136.0, 135.1, 134.1, 133.6, 130.0,

129.8, 129.2, 129.0, 128.3, 127.7, 127.3, 127.1, 125.1, 118.2, 63.6. HRMS (ESI): m/z Calcd. for $[C_{37}H_{27}N_2, L]^+$: 499.64; Found: 498.90. IR (KBr, cm^{-1}): 3060(m), 2927(w), 1671(m), 1640(s),1598(w), 1544(m), 1514(w), 1454(w), 1406(m), 1165(m), 852(s), 834(s), 762(m), 732(m), 696(w), 557(m).

L-BF_4: Excess $NaBF_4$ (100 mg) was added into a solution of **L-Cl** (150 mg) in CH_3OH (15 mL). The reaction mixture was stirred at room temperature for 12 h. The resultant yellow microcrystals with the yield of ~90% were collected by filtration and washed with CH_3OH. ^1H NMR: (400 MHz, DMSO-D6) δ: 9.49 (2 H, d, *J* 6.9), 9.04 (4 H, m), 8.72 (2 H, s), 8.62 (2 H, d, *J* 8.5), 8.16 (4 H, m), 8.04 (2 H, d, *J* 9.5), 7.63 (6 H, m), 7.49 (3 H, m), 5.95 (2 H, s). ^{13}C NMR: (400 MHz, DMSO-D6) δ: 157.7, 153.9, 145.7, 144.1, 136.0, 135.1, 134.1, 133.6, 130.0, 129.2, 128.9, 128.2, 127.6, 127.2, 127.0, 125.1, 118.2, 63.6. HRMS (ESI): m/z Calcd. for $[C_{37}H_{27}N_2, L]^+$: 499.64; Found: 498.85. IR (KBr, cm^{-1}): 3060(m), 2922(w), 1640(m), 1598(w), 1550(m), 1520 (w), 1454(w), 1406(m), 1123(m), 1081(s), 847(w), 816(m), 756(m), 732(w), 534(w).

Preparations of ionic polymers in CH_3CN

P1-Cl (mass ratios of **L**/**P** = 1:10)**: L** (0.010 g) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in CH_3CN (15 mL). The reaction mixtures were stirred at 100 °C under N_2 for 12 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving **P1-Cl** (the yield is above 90%).

P2-Cl (**L**/**P** = 1:2)**: L** (0.050 g) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in CH_3CN (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 12 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving **P2-Cl** (the yield is above 90%).

P1-PF_6 (**L**/**P** = 1:10): **L** (0.010 g) and NH_4PF_6 (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in CH_3CN (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 12 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving **P1-PF_6** (the yield is above 90%).

P2-PF_6 (**L**/**P** = 1:2): **L** (0.050 g) and NH_4PF_6 (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in CH_3CN (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 12 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving **P2-PF_6** (the yield is above 90%).

P3-PF_6 (**L**/**P** = 2:3): **L** (0.100 g) and NH_4PF_6 (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.150 g) in CH_3CN (20 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 12 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving **P2-PF_6** (the yield is above 90%).

P4-PF_6 (**L**/**P** = 1:1): **L** (0.100 g) and NH_4PF_6 (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in CH_3CN (20 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 24 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving **P2-PF_6** (the yield is above 90%).

P1-BF_4 (**L**/**P** = 1:10): **L** (0.010 g) and $NaBF_4$ (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in CH_3CN (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 12 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving **P1-BF_4** (the yield is above 90%).

P2-BF_4 (**L**/**P** = 1:2): **L** (0.050 g) and $NaBF_4$ (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in CH_3CN (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 12 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving **P2-BF_4** (the yield is above 90%).

P3-BF_4 (**L**/**P** = 2:3): **L** (0.100 g) and $NaBF_4$ (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.150 g) in CH_3CN (20 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 12 h. The resultant precipitates were collected by

filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving **P3-BF_4** (the yield is above 90%).

P4-BF_4 (**L**/**P** = 1:1): **L** (0.1000 g) and $NaBF_4$ (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.1000 g) in CH_3CN (20 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 24 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, DMF, DCM and CH_3OH, giving (the yield is above 90%).

Preparations of ionic polymers in DMF

P5-PF_6 (**L**/**P** = 1:10): **L** (0.010 g) and NH_4PF_6 (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in DMF (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 24 h. The resultant precipitates were collected by filtration and washed many times with DMF, DCM and CH_3OH, giving **P5-PF_6** (the yield is above 90%).

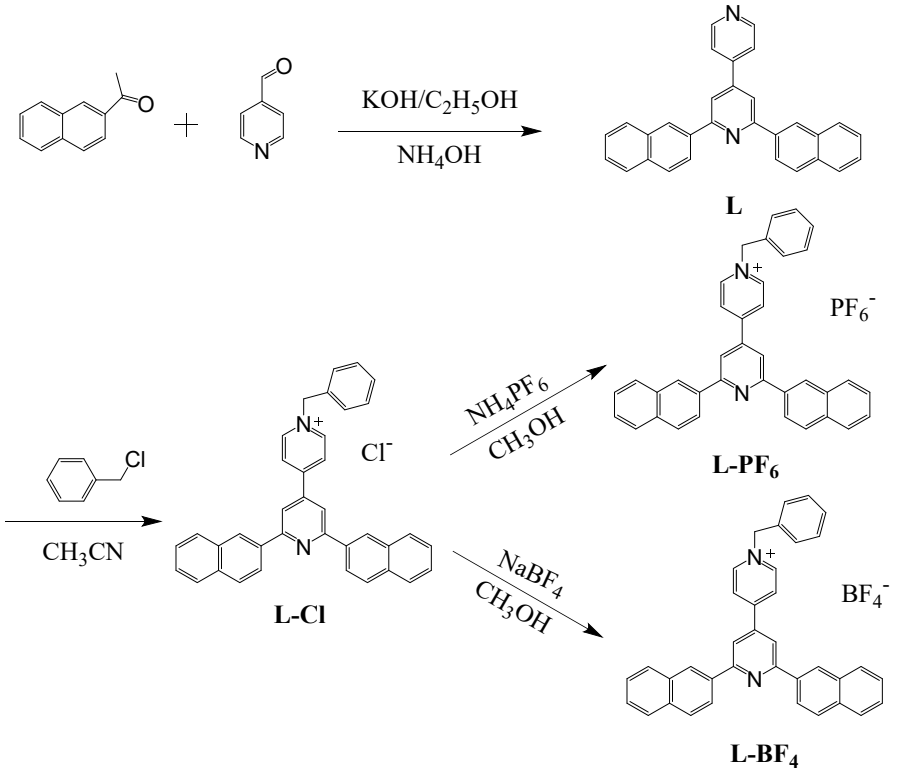
P6-PF_6 (**L**/**P** = 1:1): **L** (0.100 g) and NH_4PF_6 (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in DMF (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 24 h. The resultant precipitates were collected by filtration and washed many times with DMF, DCM and CH_3OH, giving **P6-PF_6** (the yield is above 90%).

P7-PF_6 (**L**/**P** = 2:1): **L** (0.100 g) and NH_4PF_6 (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.050 g) in DMF (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 24 h. The resultant precipitates were collected by filtration and washed many times with DMF, DCM and CH_3OH, giving **P7-PF_6** (the yield is above 90%).

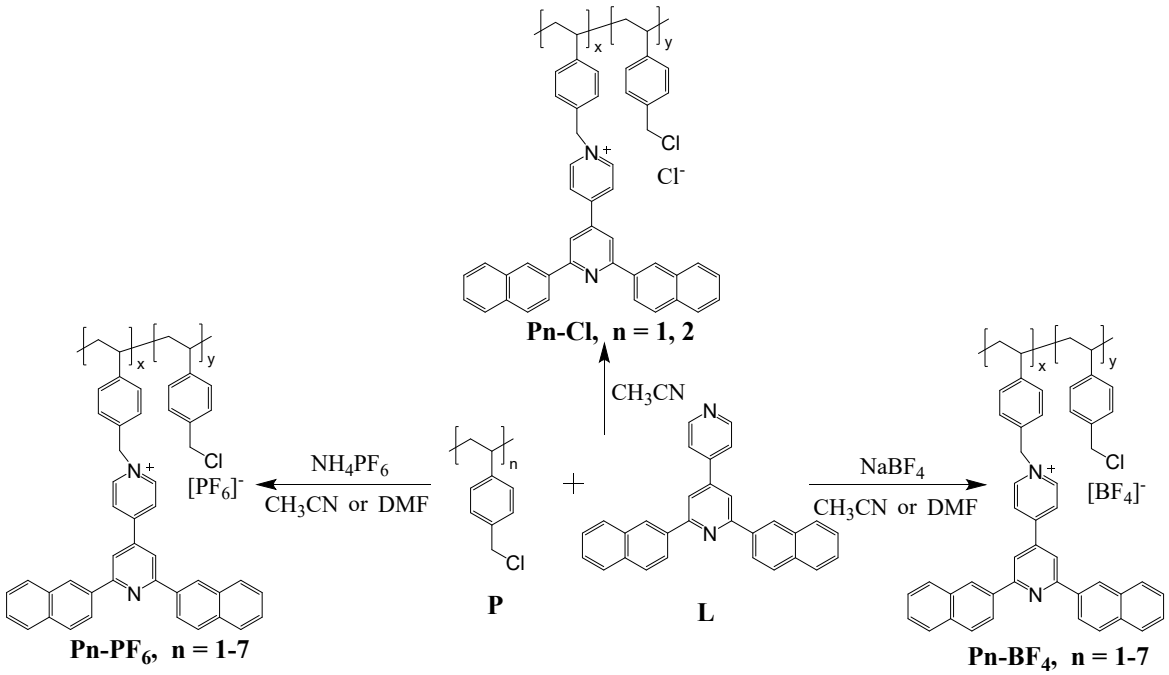
P5-BF_4 (**L**/**P** = 1:10): **L** (0.010 g) and $NaBF_4$ (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in DMF (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 24 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, CH_3OH, DCM and DMF, giving **P5-BF_4** (the yield is above 90%).

P6-BF_4 (**L/P** = 1:1): **L** (0.100 g) and $NaBF_4$ (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.100 g) in DMF (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 24 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, CH_3OH, DCM and DMF, giving **P6-BF_4** (the yield is above 90%).

P7-BF_4 (**L/P** = 2:1): **L** (0.100 g) and $NaBF_4$ (100 mg) was added into a solution of chloromethyl polystyrene resin **P** (0.050 g) in DMF (15 mL), respectively. The reaction mixtures were stirred at 100 °C under N_2 for 24 h. The resultant precipitates were collected by filtration and washed many times with CH_3CN, CH_3OH, DCM and DMF, giving **P7-BF_4** (the yield is above 90%).



Scheme S1. Synthetic routes of **L, L-Cl, L-PF_6 and L-BF_4**.



Scheme S2. The general synthetic routes of ionic polymers containing different anions.

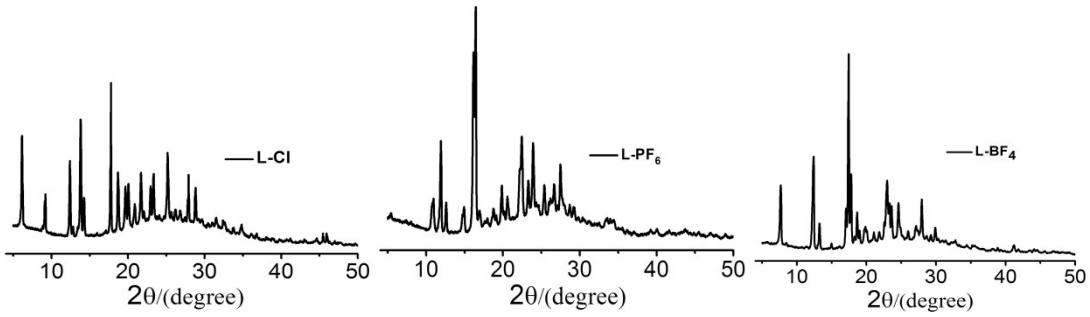


Fig. S1 X-ray powder diffractions of **L-Cl**, **L-PF$_6$** and **L-BF$_4$** in the crystalline states. Those crystalline samples have been obtained by slowly diffusing ether into their corresponding solution.

Table S1 The optical properties of **L**, **L-Cl**, **L-BF$_4$**, **L-PF$_6$** in the different states

Sample	Solution		Solid	
	λ_{em} (nm)	quantum yield (%)	λ_{em} (nm)	quantum yield (%)
L	390	29.2	418	25.0
L-Cl	625	1.0	477	29.5
	508 (add H_2O)	10.6		
L-BF$_4$	635	0.9	529	84.6
	521 (add H_2O)	4.9		
L-PF$_6$	638	0.8	548	48.0
	553 (add H_2O)	5.0		

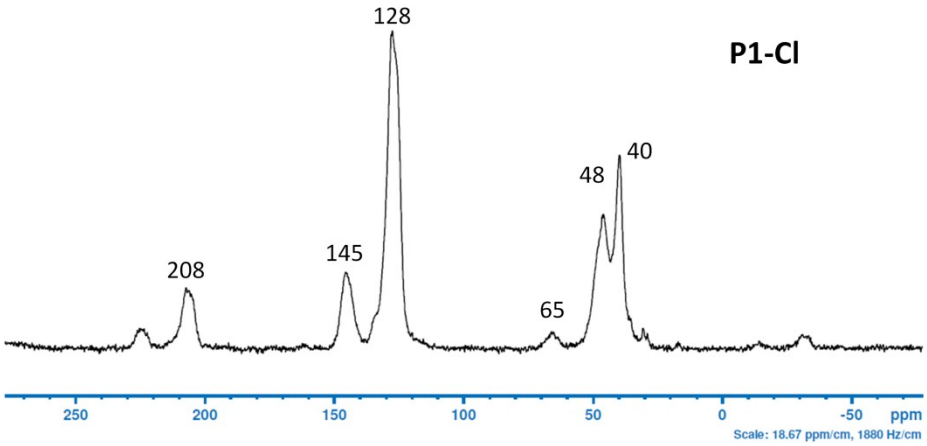


Fig. S2 Solid state ^{13}C NMR spectrum of **P1-Cl**

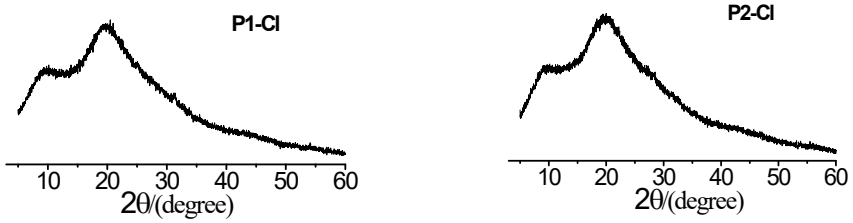


Fig. S3 X-ray powder diffractions of **P1-Cl** and **P2-Cl**.

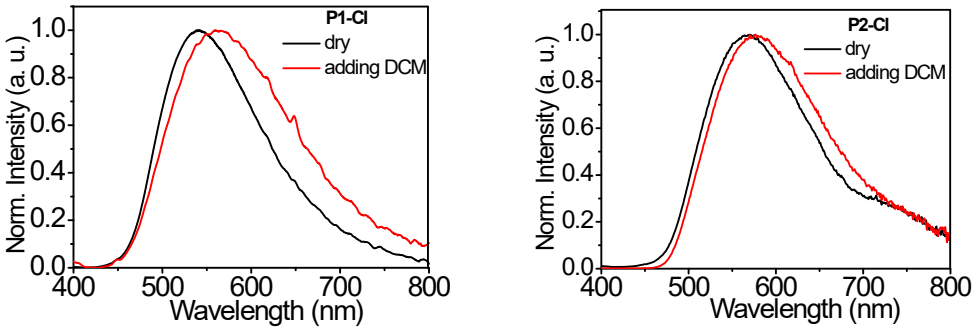


Fig. S4 Emission spectra of **P1-Cl** and **P2-Cl** before and after adding DCM, respectively.

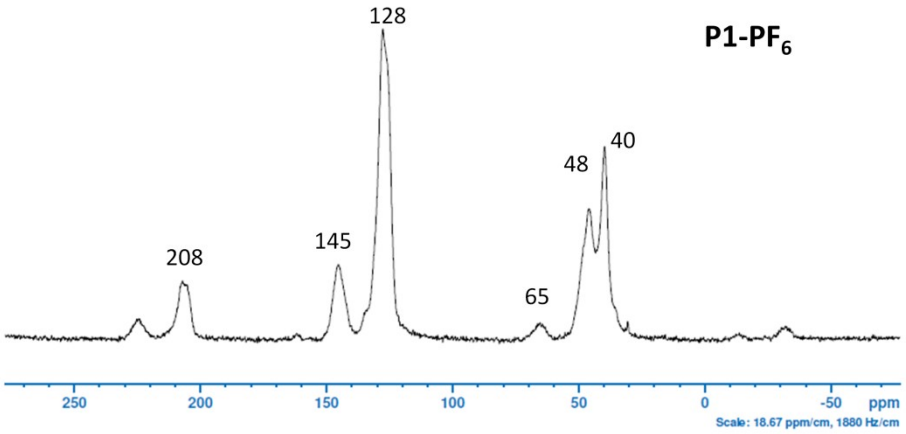


Fig. S5 Solid state ^{13}C NMR spectrum of **P1-PF$_6$**

Fig. S6 X-ray powder diffractions of **P1-PF$_6$** and **P1-BF$_4$**.

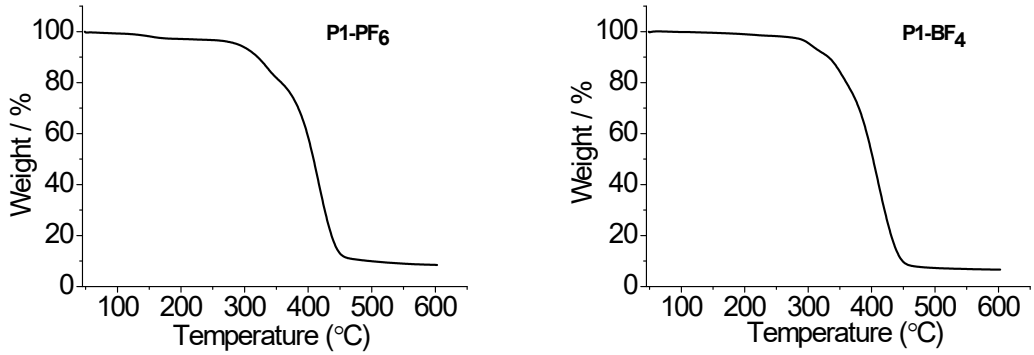


Fig. S7 The TGA curves of **P1-PF$_6$** and **P1-BF$_4$**.

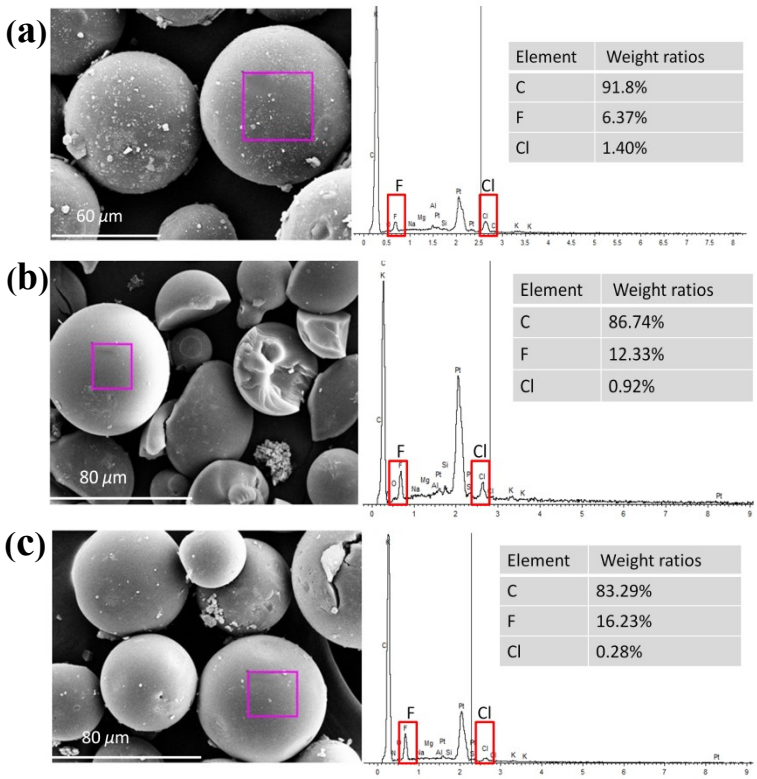


Fig. S8 The scanning electron microscope energy dispersive spectrometer analysis (SEM-EDS) of (a) **P1-PF$_6$**, (b) **P2-PF$_6$** and (c) **P4-PF$_6$**.

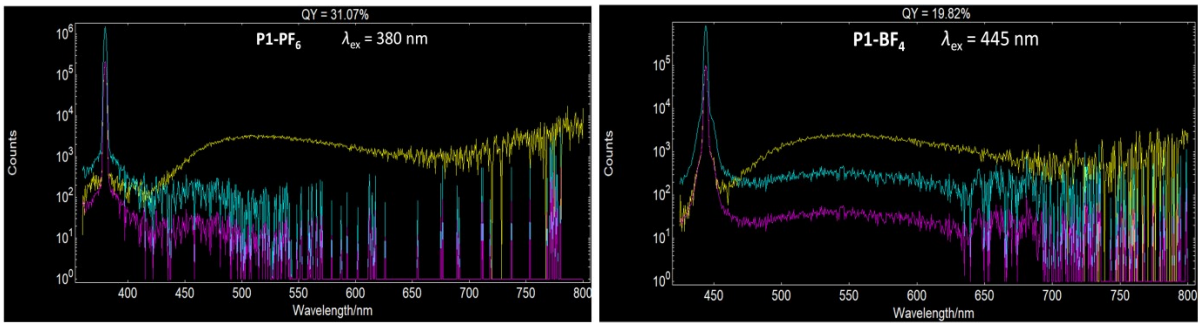


Fig. S9 Quantum yields of **P1-PF$_6$** and **P1-BF$_4$**.

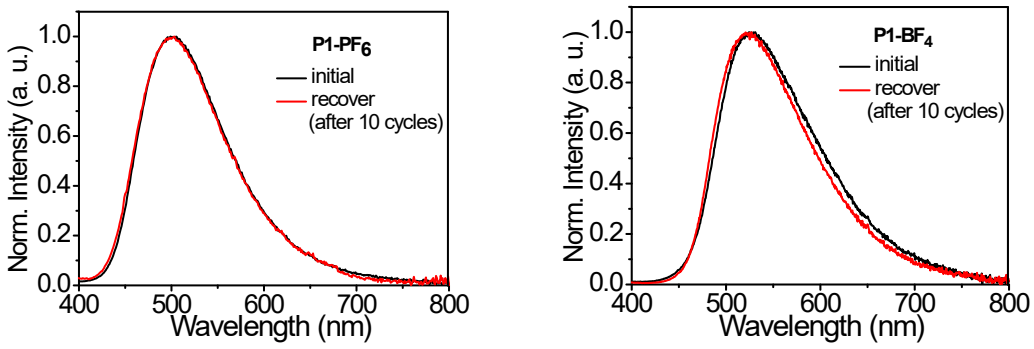


Fig. S10 The emission spectra of **P1-PF$_6$** and **P1-BF$_4$** under 365 nm excitation after 10 cycles of DCM uptake and release, respectively.

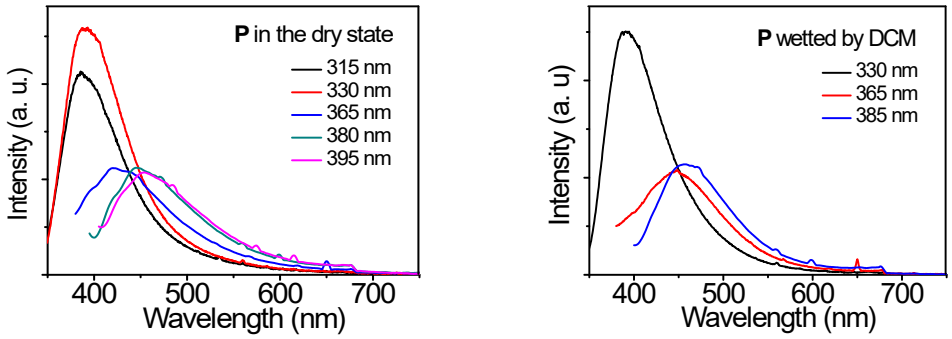


Fig. S11 Emission spectra of **P** in the dry state and **P** wetted by DCM under the different excitation wavelengths, respectively.

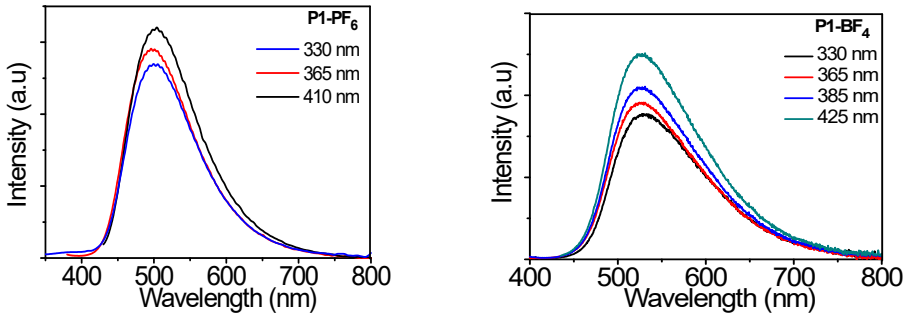


Fig. S12 Emission spectra of **P1-PF$_6$** and **P1-BF$_4$** in the dry states under the different excitation wavelengths, respectively.

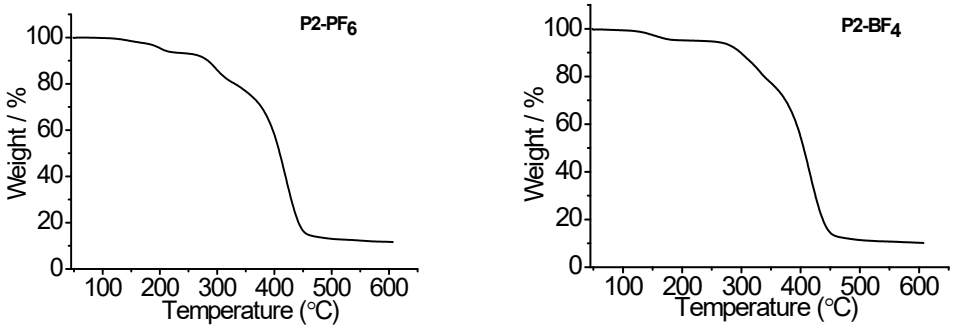


Fig. S13 The TGA curves of **P2-PF$_6$** and **P2-BF$_4$**.

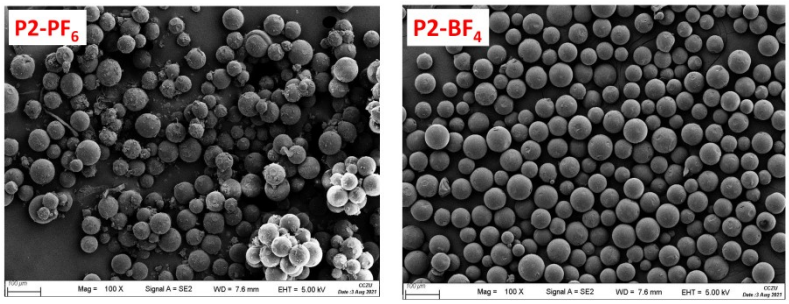


Fig. S14 SEM images of **P2-PF$_6$** and **P2-BF$_4$**.

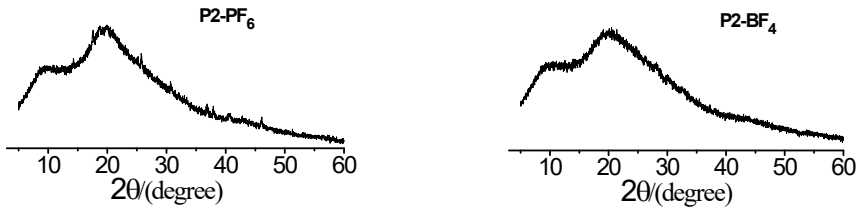


Fig. S15 X-ray powder diffractions of **P2-PF$_6$** and **P2-BF$_4$**.

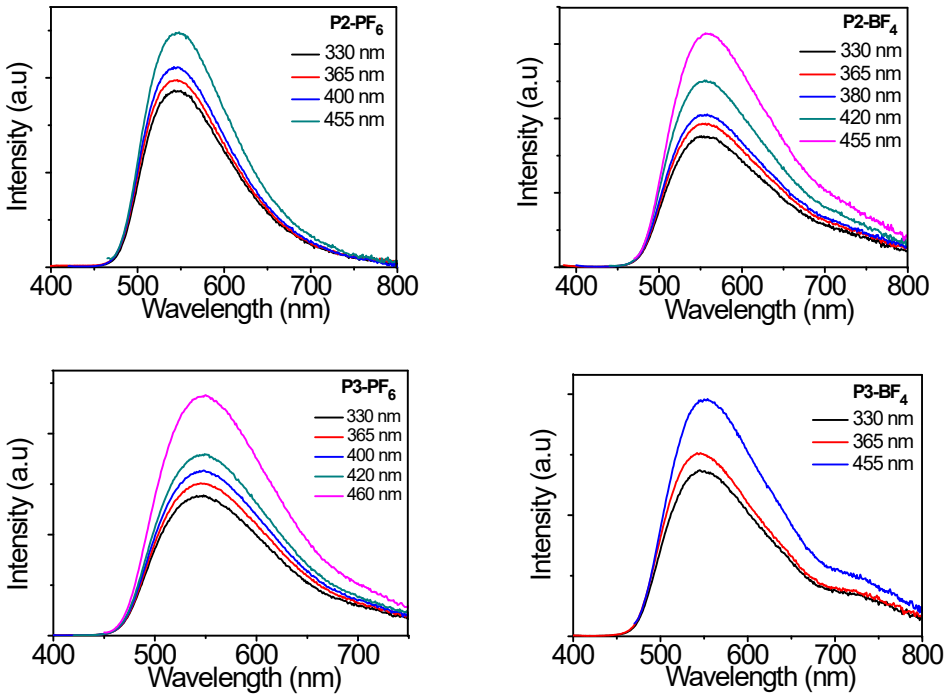


Fig. S16 Emission spectra of ionic polymers (**P2-PF$_6$**, **P2-BF$_4$**, **P3-PF$_6$**, **P3-BF$_4$**) in the dry states under different excitation wavelengths, respectively.

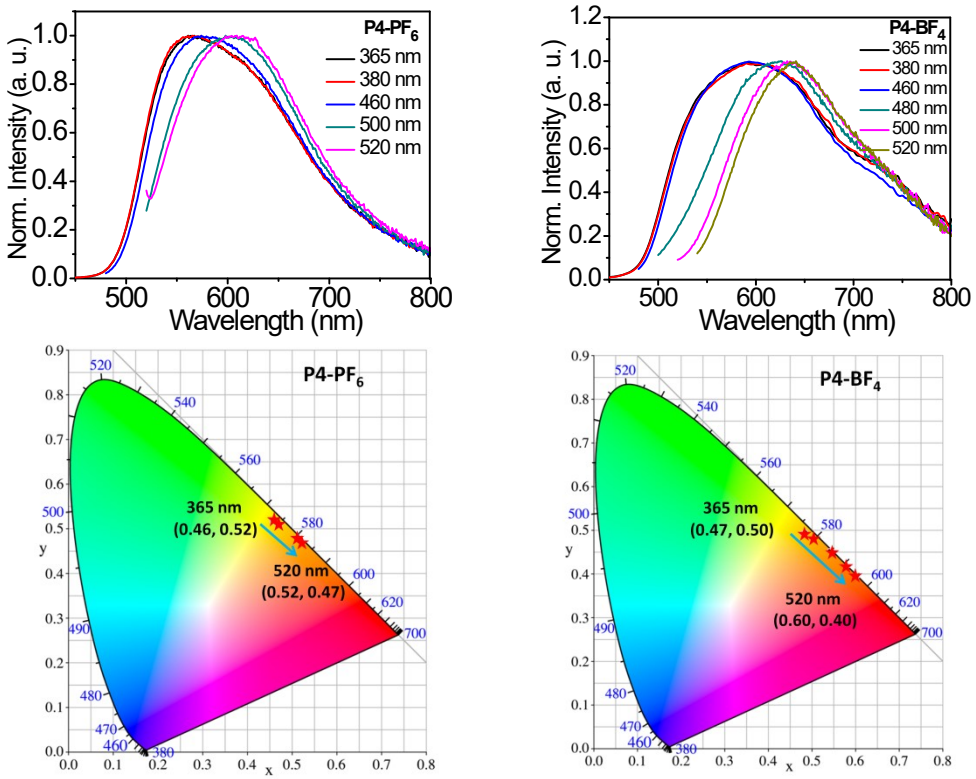


Fig. S17 Emission spectra of ionic polymers (**P4-PF_6**, **P4-BF_4**) under the different excitation wavelengths and the corresponding CIE coordinates.

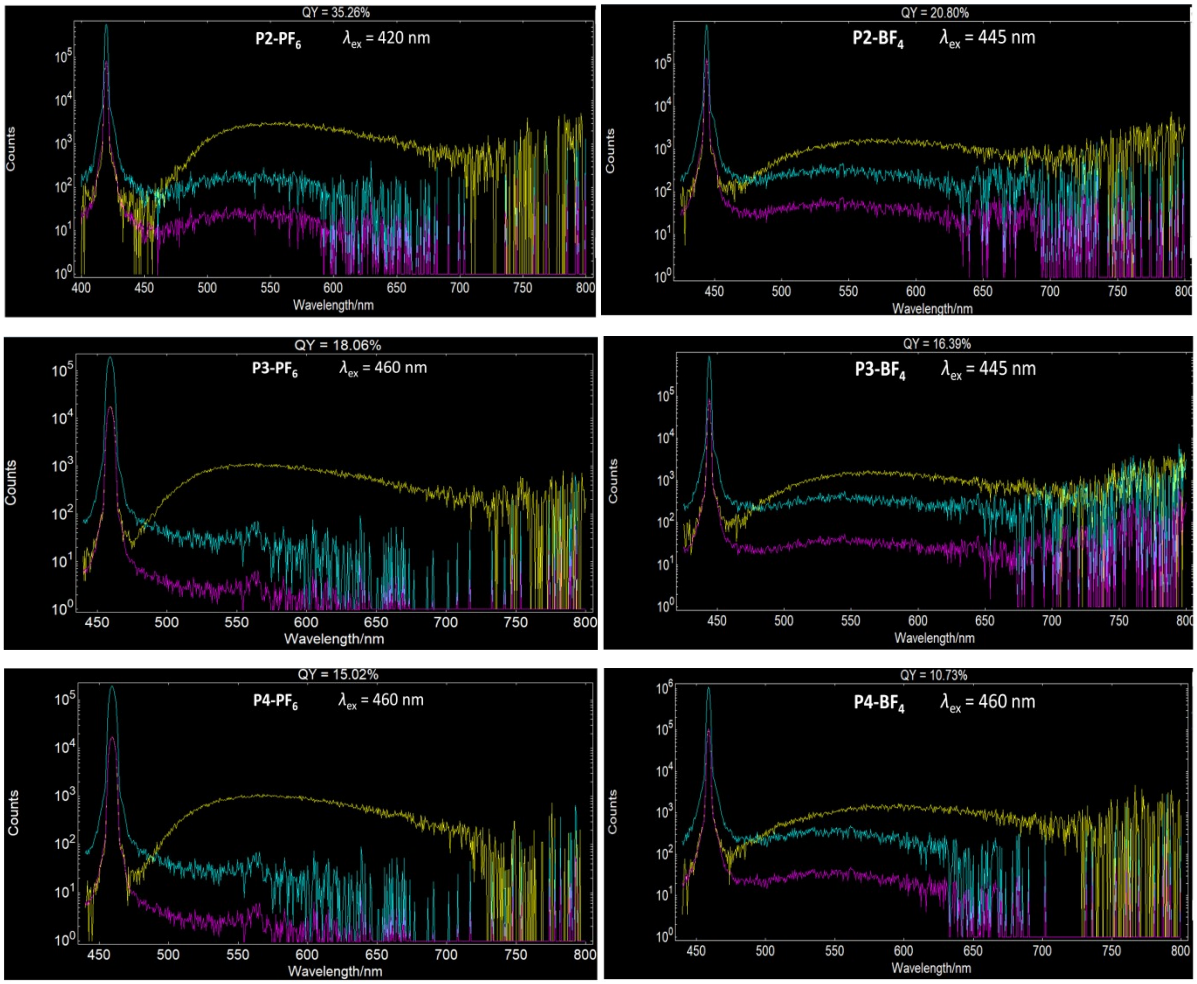


Fig. S18 Quantum yields of **P2-PF$_6$**, **P2-BF$_4$**, **P3-PF$_6$**, **P3-BF$_4$**, **P4-PF$_6$**, **P4-BF$_4$**.

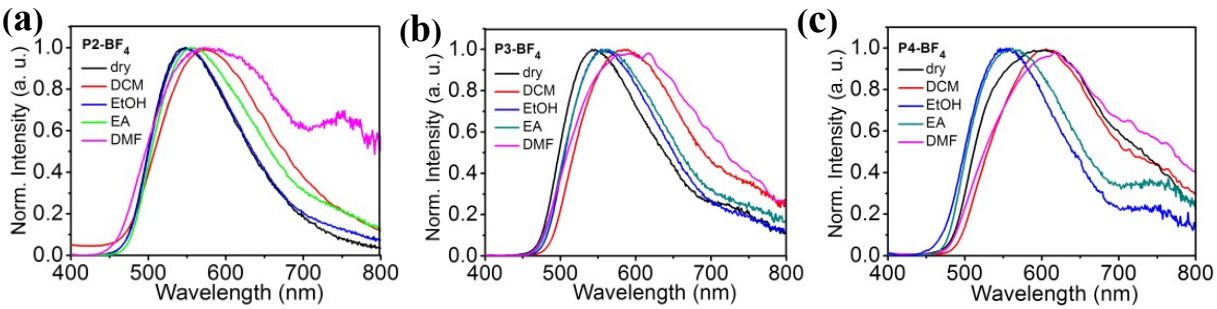


Fig. S19 Emission spectra of (a) **P2-BF$_4$**, (b) **P3-BF$_4$** and (c) **P4-BF$_4$** in the dry states and the various wetted states responded to the different solvents.

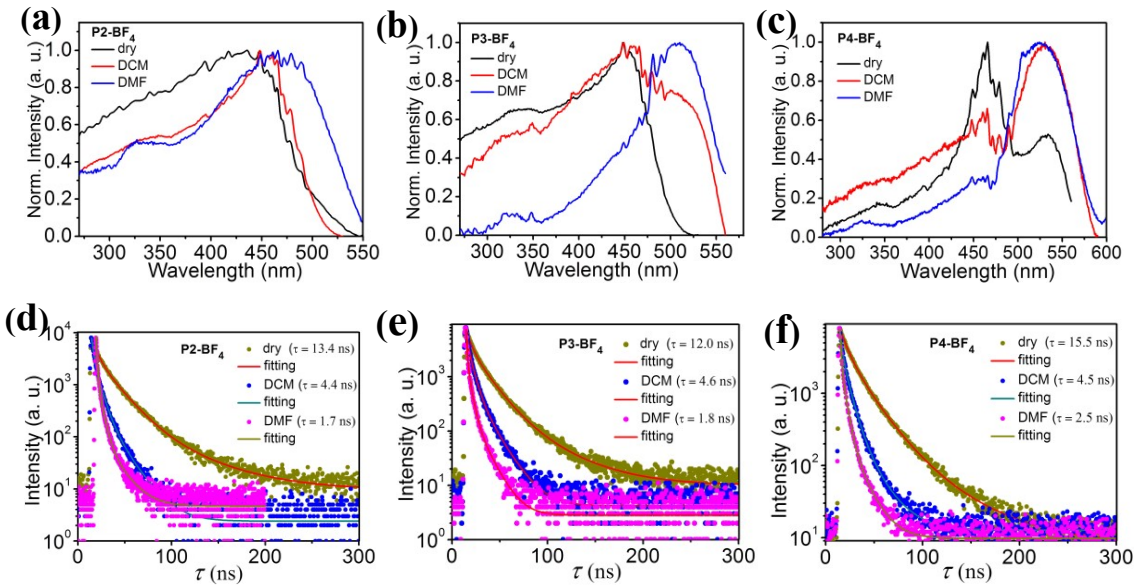


Fig. S20 a-c) Excitation spectra of those ionic polymers (**P2-BF$_4$**, **P3-BF$_4$**, **P4-BF$_4$**) in the dry states, the wetted states with DCM and the wetted states with DMF; d-f) Emission lifetimes of those ionic polymers (**P2-BF$_4$**, **P3-BF$_4$**, **P4-BF$_4$**) in the dry states, the wetted states with DCM and the wetted states with DMF.

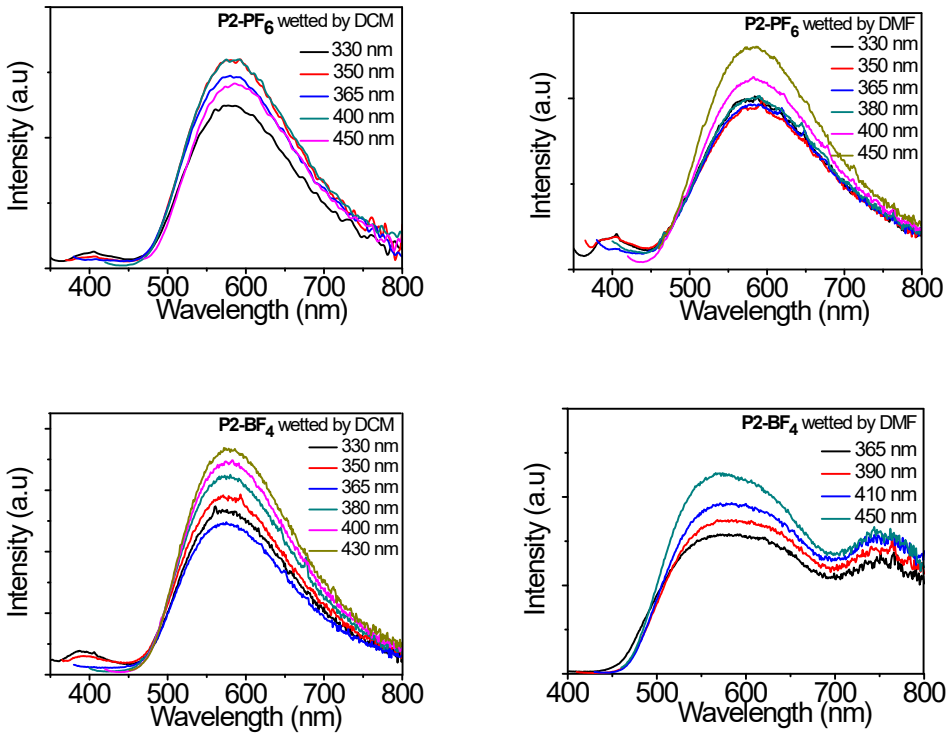


Fig. S21 Emission spectra of ionic polymers (**P2-PF$_6$**, **P2-BF$_4$**) in the wetted states with DCM and the wetted states with DMF under the different excitation wavelengths.

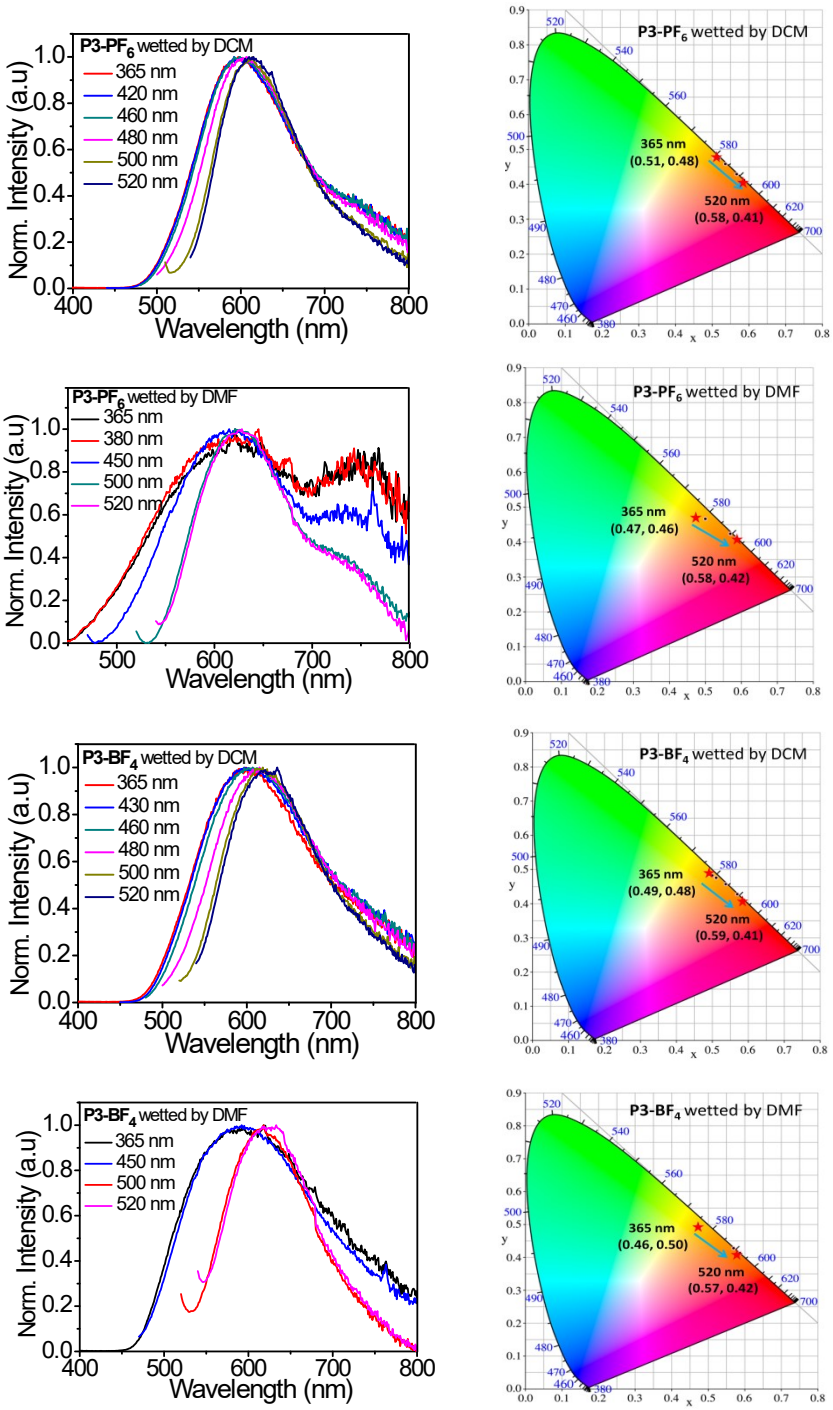


Fig. S22 Emission spectra of ionic polymers (**P3-PF_6**, **P3-BF_4**) in the wetted states with DCM and the wetted states with DMF under the different excitation wavelengths, and their corresponding CIE coordinates, respectively.

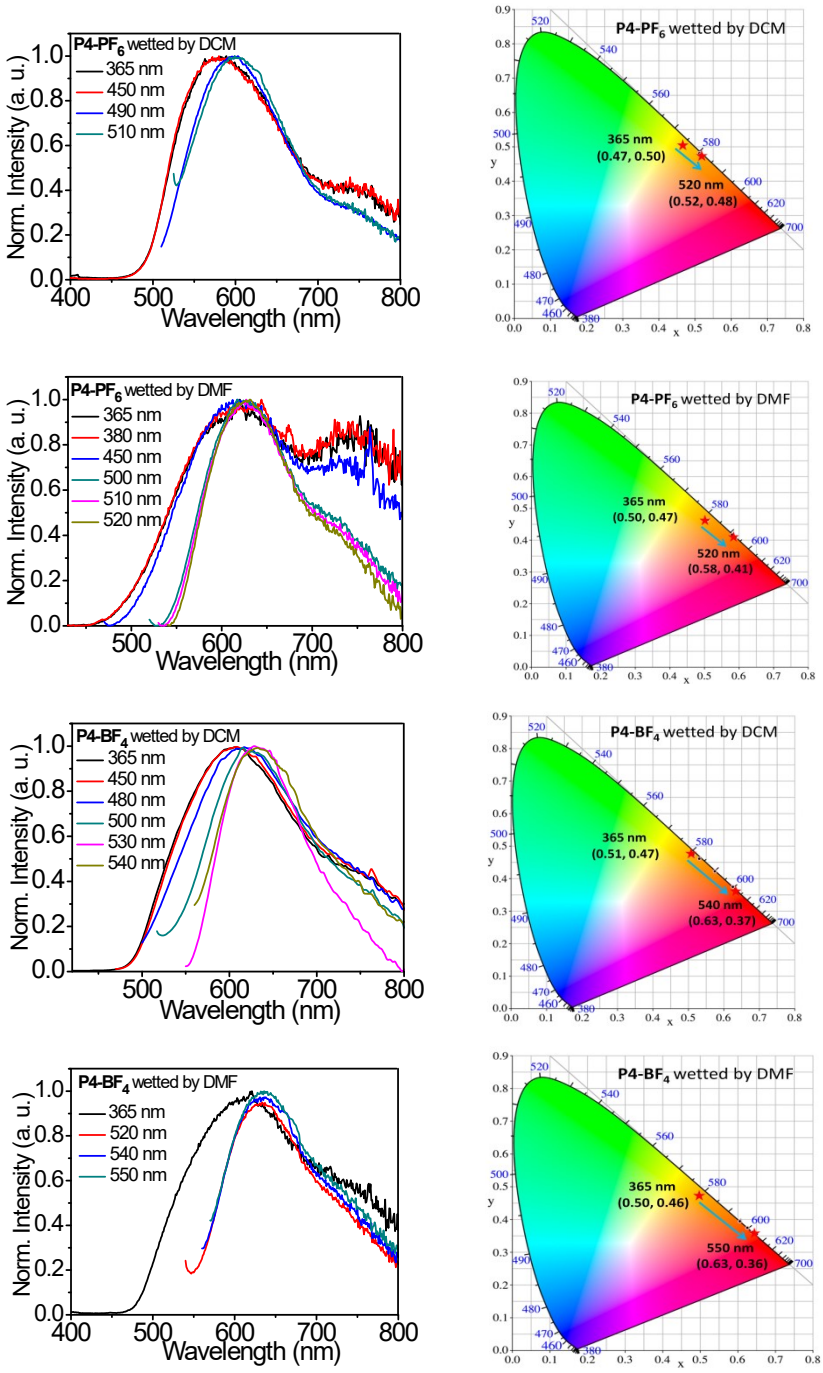


Fig. S23 Emission spectra of ionic polymers (**P4-PF_6**, **P4-BF_4**) under the different excitation wavelengths in the wetted states with DCM and the wetted states with DMF, and their corresponding CIE coordinates, respectively.

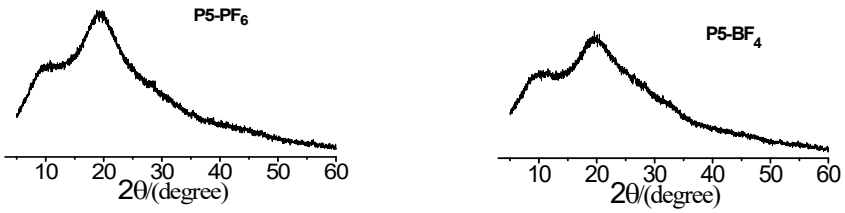


Fig. S24 X-ray powder diffractions of **P5-PF$_6$** and **P5-BF$_4$**.

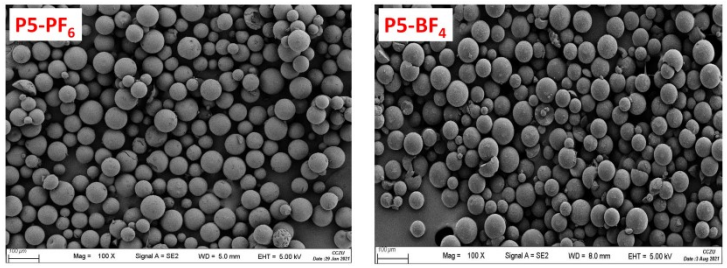


Fig. S25 SEM images of **P5-PF$_6$** and **P5-BF$_4$**.

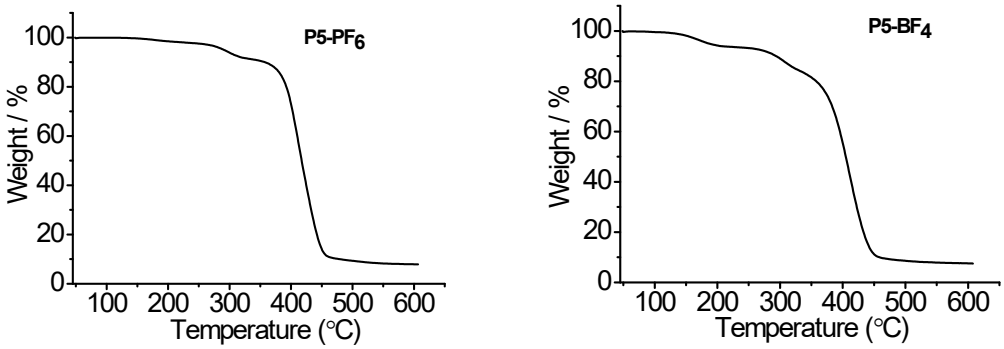


Fig. S26 The TGA curves of **P5-PF$_6$** and **P5-BF$_4$**.

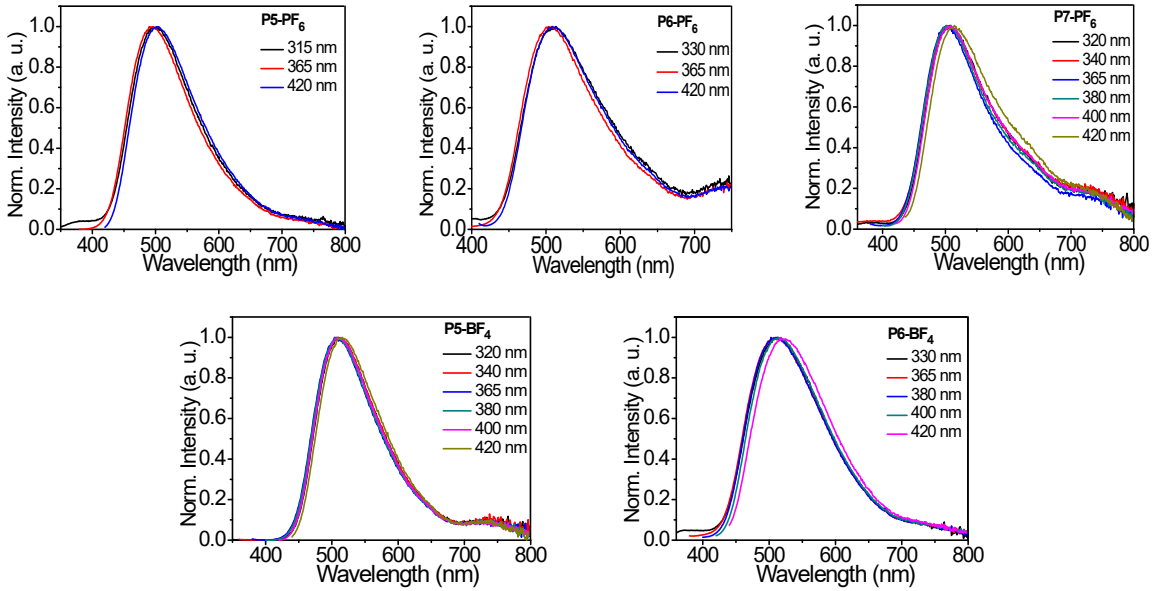


Fig. S27 Emission spectra of ionic polymers (**P5-PF$_6$**, **P5-BF$_4$**, **P6-PF$_6$**, **P6-BF$_4$**, **P7-PF$_6$**) in the dry states under the different excitation wavelengths.

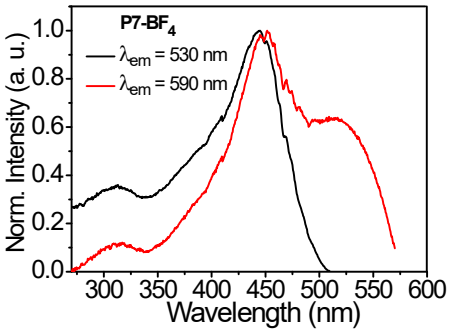


Fig. S28 Excitation spectra of **P7-BF$_4$** in the dry state for emission peaks at 530 nm and 590 nm.

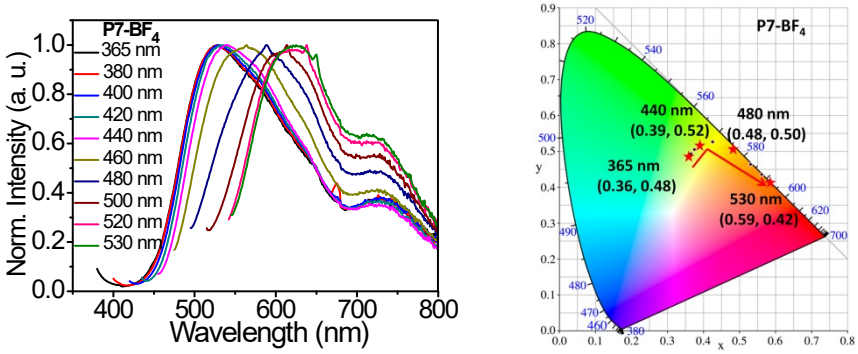


Fig. S29 Emission spectra of **P7-BF$_4$** in the dry state under the different excitation wavelengths and the corresponding CIE coordinates.

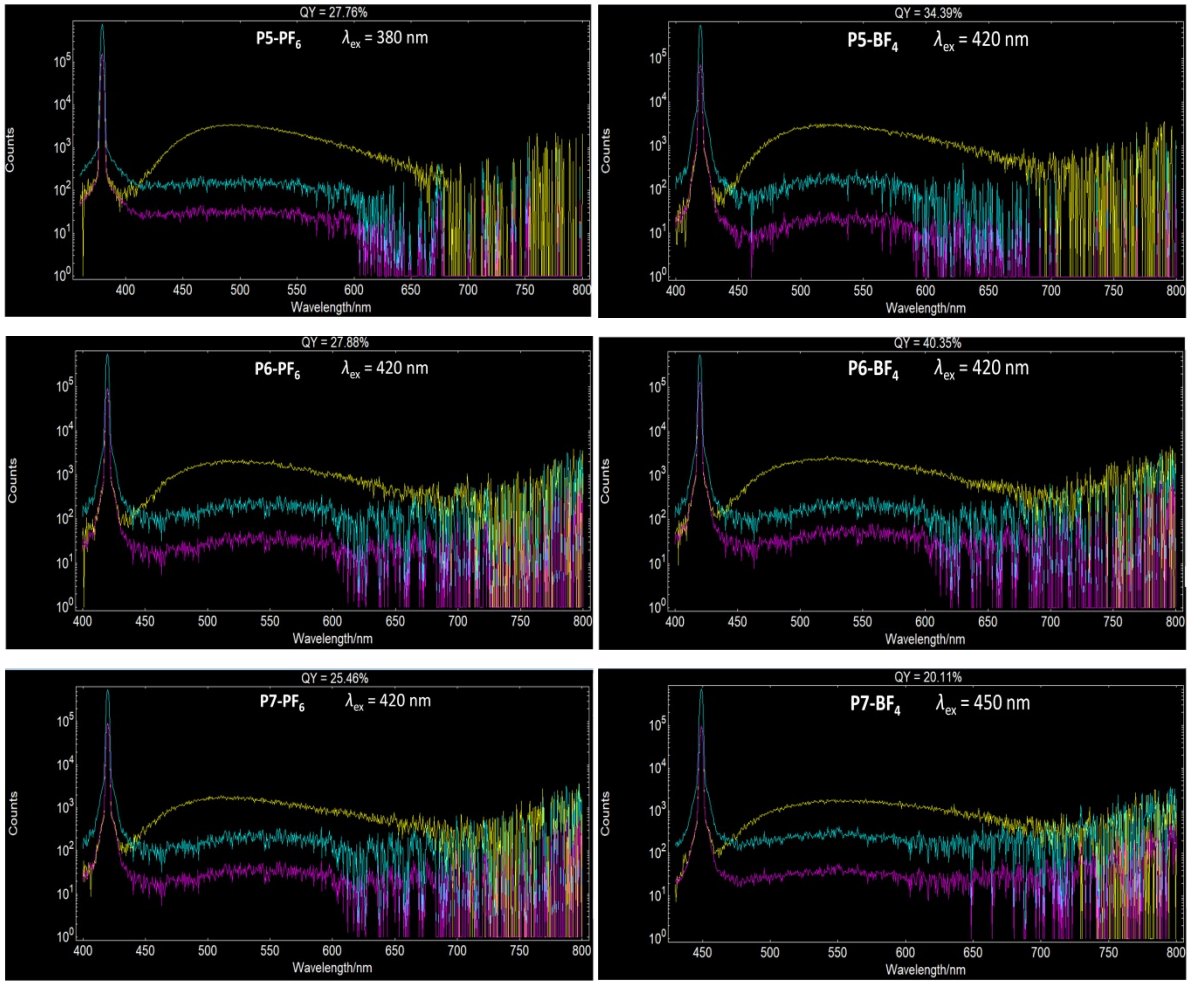


Fig. S30 Quantum yields of **P5-PF$_6$**, **P5-BF$_4$**, **P6-PF$_6$**, **P6-BF$_4$**, **P7-PF$_6$**, **P7-BF$_4$**.

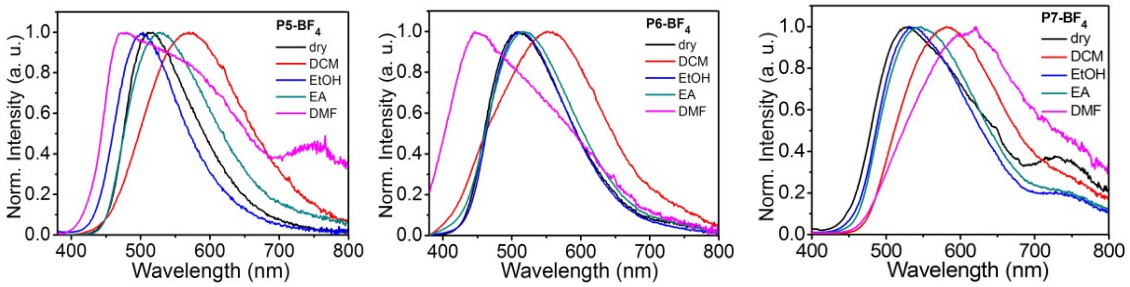


Fig. S31 Emission spectra of ionic polymers (**P5-BF$_4$**, **P6-BF$_4$**, **P7-BF$_4$**) in the dry states and the various wetted states responded to the different solvents.

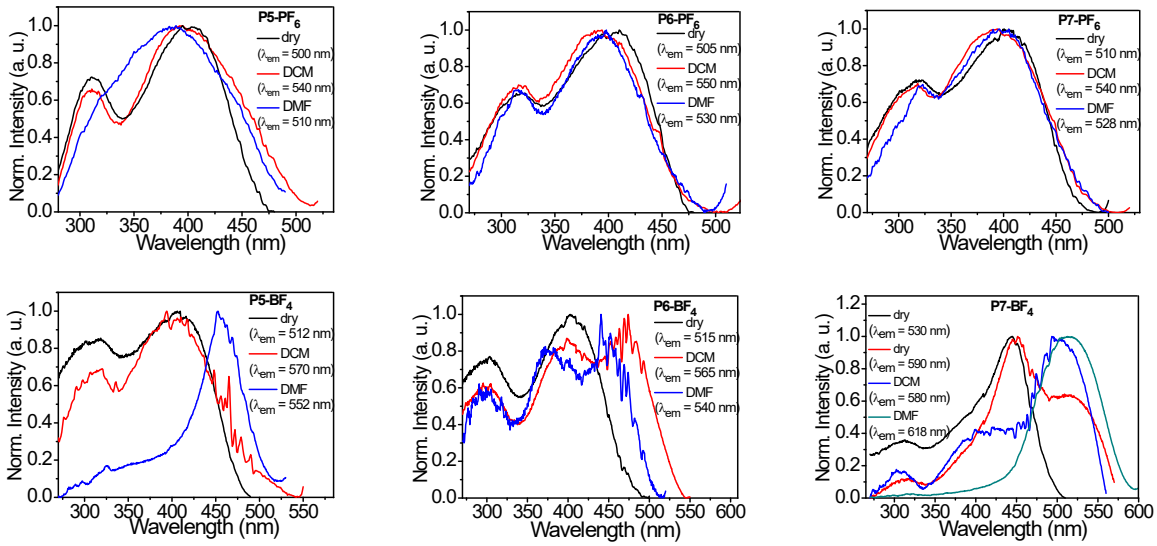


Fig. S32 Excitation spectra of ionic polymers (**P5-PF$_6$**, **P5-BF$_4$**, **P6-PF$_6$**, **P6-BF$_4$**, **P7-PF$_6$**, **P7-BF$_4$**) in the dry states, the wetted states with DCM and the wetted states with DMF, respectively.

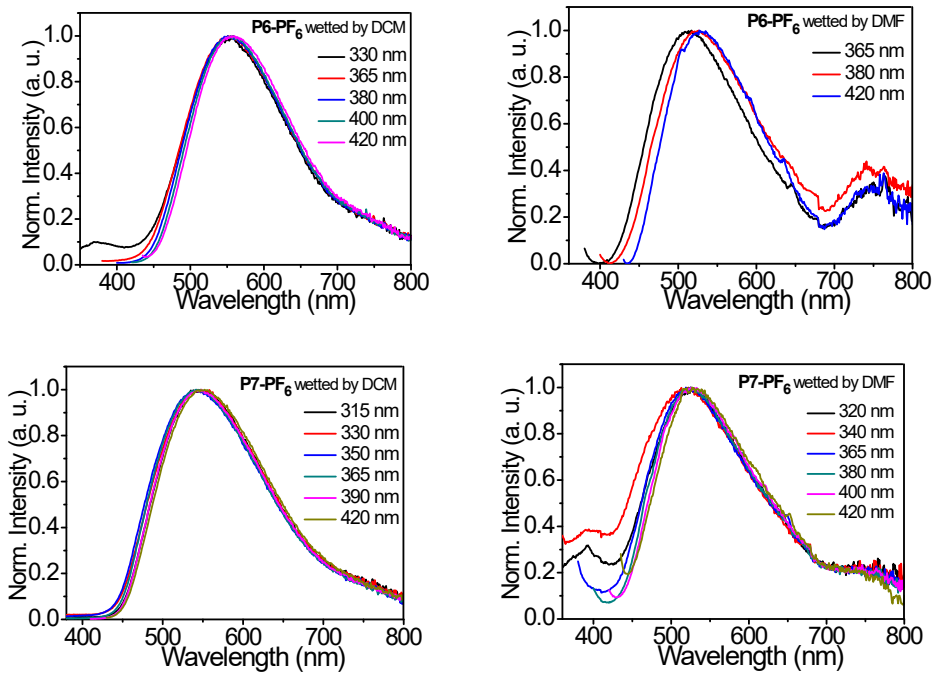


Fig. S33 Emission spectra of ionic polymers (**P6-PF$_6$**, **P7-PF$_6$**) in the wetted states with DCM and the wetted states with DMF under the different excitation wavelengths, respectively.

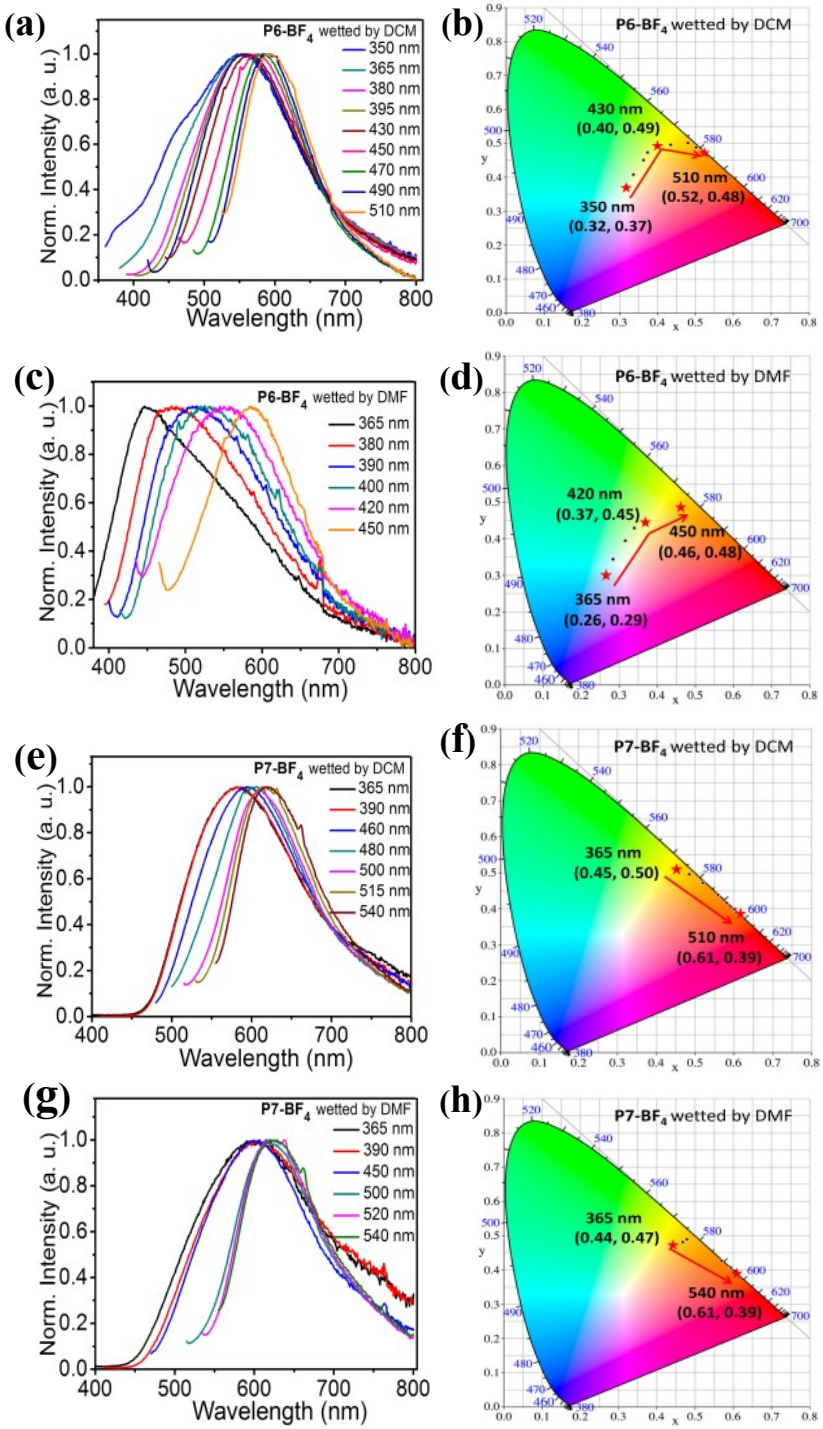


Fig. S34 a, c, e, g) Emission spectra of ionic polymers (**P5-PF$_6$**, **P5-BF$_4$**, **P6-BF$_4$**, **P7-BF$_4$**) in the wetted states with DCM and the wetted states with DMF under the different excitation wavelengths, respectively; b, d, f, h) Their corresponding CIE coordinates.