

Supporting Information

Construction of Coordination Nanosheets Based on Tris(2,2'-bipyridine)-Iron(Fe^{2+}) Complexes as Potential Electrochromic Materials

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Section S-1: Materials and Instrumentation

Materials

All chemicals, and solvents for synthesis purpose were purchased from Aldrich Chemical Co., TCI Co., Wako, and Kanto Chemical Co. Inc. Indium tin oxide (ITO) coated glass substrate (resistivity 8-12 Ω/sq) was purchased from Aldrich Chemical Co. All ITO substrates were cleaned by ultrasonication with ethanol and acetone for 10 min followed by exposure to ultraviolet-ozone for 30 min. Anhydrous grade solvents were used for organic synthesis and spectrophotometric grade solvents were used for film preparation, spectroscopic study, and device fabrication. Purified water by Milli-Q purification system was used in the experiment where it was required. Compounds **3**,¹⁻² **4**,³ **5**,⁴⁻⁵ and **BP1**³ were prepared according to literature procedures.

General instrumentations and methods

Nuclear Magnetic Resonance (NMR) spectroscopy

¹H-NMR spectra were recorded at 300 MHz on a JEOL AL 300/BZ instrument using CDCl₃ and DMSO-d₆ as the solvent. Chemical shifts are given here relative to tetramethylsilane (TMS) and expressed in parts per million (ppm).

Matrix assisted laser desorption ionization-time of flight mass (MALDI-TOF) spectrometry

MALDI-TOF mass spectra were measured by using AXIMA-CFR, Shimadzu/Kratos TOF mass spectrometer using 1,8,9-trihydroxyanthracene as a matrix.

UV-vis spectroscopy

The UV-vis spectra were recorded using a Shimadzu UV-2550 UV-visible spectrophotometer. For ligands **BP1** and **BP2**, spectra were recorded in dichloromethane (DCM) solution (5×10^{-6} M) and for **NBP1** and **NBP2**, spectra were recorded using the film on ITO substrate. The UV-vis spectrum of monolayer was measured using a photodiode array-equipped spectrometer (Otsuka Electronics, model MCPD-9800). The incident light through an optical fiber was directed at an angle of 60° against the water surface, and absorption was detected by an optical fiber positioned in parallel.

Fourier transform infrared (FT-IR) spectroscopy

The FT-IR measurements were carried out by Nicolet 4700 FT-IR spectrophotometer equipped with a Mercury-Cadmium Telluride (MCT) detector and transmittance measurement was monitored using KBr-disk.

Raman spectroscopy

Raman measurements were performed at room temperature with a Jobin-Yvon T64000 triple monochromator spectrometer equipped with a liquid N₂-cooled CCD detector.

Powder X-ray diffraction (PXRD)

The PXRD measurement was done by using a RINT ULTIMA III device with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$), a generator voltage of 40 kV, and a current of 40 mA. The CONASHs powder was placed on a glass holder and scanned in a range of $2\theta = 2-60^\circ$ at a scan rate of 1 s per step with a step width of 0.01° at room temperature.

Optical microscopy (OM)

The OM analysis was carried out using OLYMPUS-BX53 microscopy attached with moticam2500 CCD camera.

Scanning electron microscopy (SEM)

The SEM analysis was carried out using S8000, Hitachi, Tokyo, Japan instrument operated at 10kV after sputter-coating using a platinum coater (E-1030 ion sputter, Hitachi, Tokyo, Japan). Samples for FE-SEM were prepared by drop casting a suspension of the nanosheets flakes in DCM and ethanol (1:1) onto a freshly cleaved silicon wafer.

Transmission electron microscopy

The TEM analysis was carried out using a JEOL JEM 2100F HRTEM. Samples for TEM were prepared by drop casting a suspension of nanosheets flakes in DCM and ethanol (1:1) on a 150-mesh carbon coated copper grid and dried under vacuum overnight.

Atomic force microscopy (AFM)

The AFM measurements were done using Seiko Instruments, Inc. (SII) (Model SPI 3800 N) in dynamic force mode (DFM), and micro cantilevers (Seiko Instruments Inc., Japan) in tapping mode with a scan rate of 0.5 Hz under air at room temperature. Samples for AFM study were prepared by spin coating a suspension of nanosheets flakes in DCM and ethanol (1:1) on silicon wafer and dried in room temperature.

Elemental analysis

The elemental analysis was performed on Elementar vario MICRO cube.

XPS

XPS spectra were recorded by PHI Quantera SXM (ULVAC-PHI) instrument using X-ray (Al K α mono) 1.4×0.1 mm 100 W (20 kV, 5 mA), take off angle: 45deg, survey spectra: pass energy 280

eV, energy step 0.5 eV. Energy calibration; C1s peak as 285.0 eV. The atomic concentrations were calculated using the survey spectra.

Electrochemical and electrochromic (EC) analysis

All electrochemical and spectroelectrochemical measurements were carried out on an ALS/CHI electrochemical workstation (CH Instruments, Inc.). A conventional three-electrode system (CONASH deposited ITO substrate as the working electrode, platinum flag as the counter electrode, and Ag/AgCl as the reference electrode) was used for CV measurement. The EC measurements were done by monitoring the transmittance change of the film upon chronoamperometry measurement in an Ocean Optics modular spectrometer. The electrochromic CIE chromaticity diagram of the devices was estimated by measuring reflection of the color.

Theoretical calculation

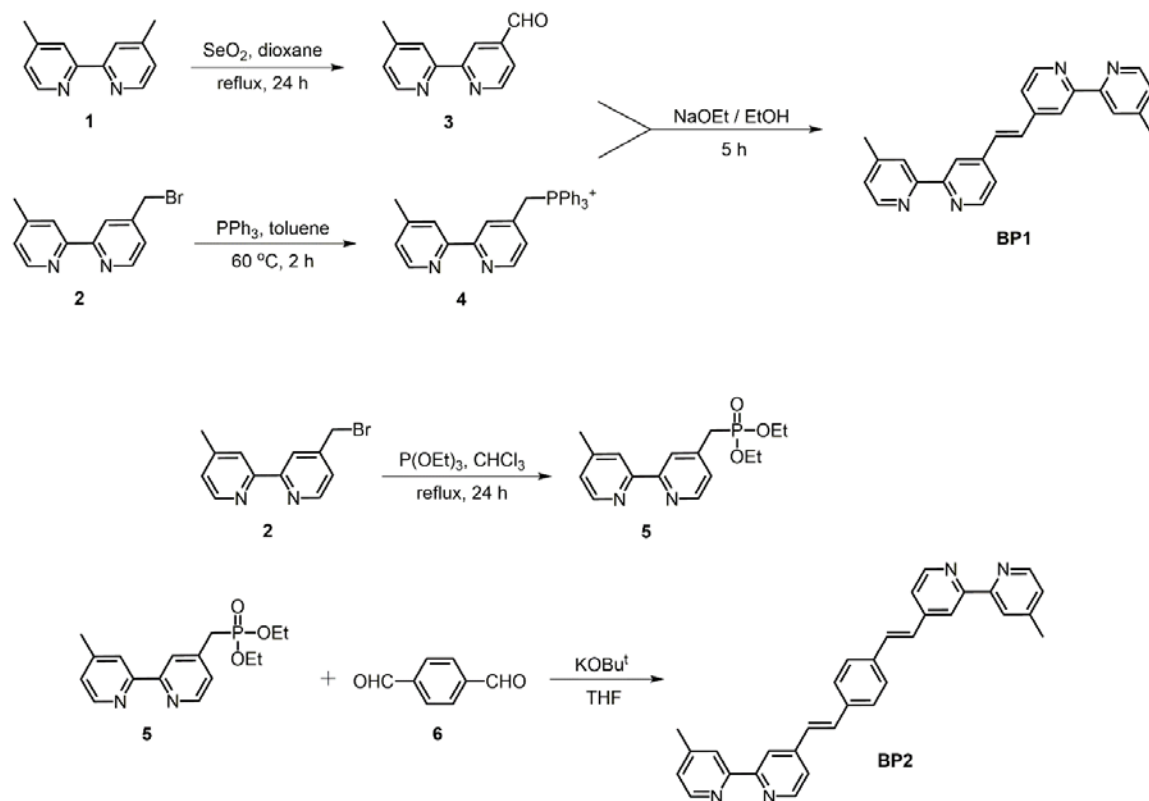
Theoretical calculation was performed by density functional theory (DFT) calculations using Gaussian09 suite of quantum chemistry program at B3LYP/6-31G (d) level.^{6,7}

Preparation of semi-gel electrolyte and fabrication of electrochromic devices

(i) The semi-gel electrolyte was prepared by mixing LiClO_4 (0.9 g) with propylene carbonate (6 mL) and acetonitrile (21 mL) followed by the addition of poly(methylmethacrylate) (PMMA; 2.1 g) under vigorous stirring. The mixture was stirred at room temperature (24 h) until the matrix polymer dissolved completely. A colorless, transparent semi-gel electrolyte was obtained as a viscous liquid. (ii) The semi-gel electrolyte was placed on an ITO substrate that was used as the counter electrode and dried for 24 h. (iii) Another ITO substrate containing CONASH film was used as the working electrode. (iv) Finally, the two ITO substrates were sandwiched to fabricate

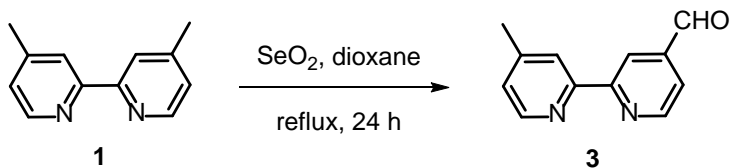
the device (dimension of the device: 2×1.5 cm). A voltage of ± 2.5 V was applied to the positive and negative electrodes of the device using a DC voltage regulator.

Section S-2: Synthetic procedures



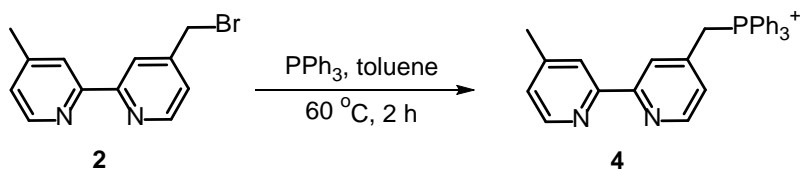
Scheme S1. Details of step wise synthesis of **BP1** and **BP2**.

Synthesis of compound 3



Dioxane (50 mL) was added to compound **1** (1.8 g, 9.7 mmol) in a 100 mL round bottomed flask and the solution was purged with nitrogen for 15 minutes. Selenium dioxide (1.1 g, 9.9 mmol) was added to the flask and the nitrogen purging was continued for an additional 20 minutes. The solution was then heated to reflux for 24 hours and solid selenium metal was precipitated on the sides of the flask with progress of reaction. After the solution cooled to room temperature it was gravity filtered and the solvent was removed under reduced pressure to get solid product which was dissolved in ethyl acetate, heated at reflux for one hour and gravity filtered while hot. Next, the filtrate was washed with 0.1 M sodium carbonate (2×30 mL) to extract any acid bipyridine formed and then extracted into a solution of 0.3 M sodium metabisulfite. The pH of the extract solution was adjusted to 10 by adding solid sodium bicarbonate, the product was extracted into dichloromethane (DCM). Solvent was evaporated under reduced pressure to give compound **3** (0.82 g, 43% yield). **¹H-NMR** (300 MHz, CDCl₃) δ (ppm): 10.19 (s, 1H), 8.91 (d, 1H), 8.84 (s, 1H), 8.59 (d, 1H), 8.28 (s, 1H), 7.74 (d, 1H), 7.21 (d, 1H), 2.47 (s, 3H). **MALDI-TOF** (m/z): calculated for [M+H]⁺: 198.23, found: 198.87.

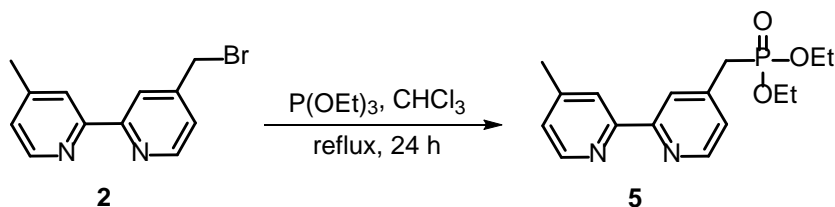
Synthesis of compound **4**



Compound **2** (0.1 g, 0.38 mmol) and excess PPh₃ (1 g, 3.8 mmol) were added to toluene (5 mL) and the solution heated at 60 °C for 2 h. The mixture was cooled to room temperature and filtered. The residue was washed with toluene and dried in vacuum for overnight to get compound **4** (0.152 g, 90 % yield) which can be used without further purification. **¹H-NMR** (300 MHz, DMSO-d₆) δ

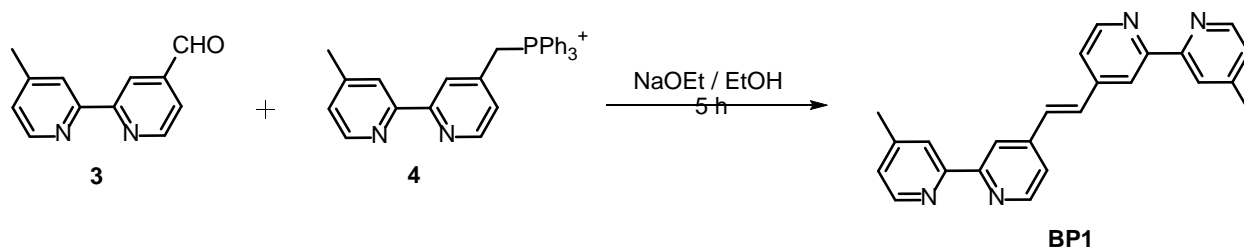
(ppm): 8.54 (d, 1H), 8.41 (d, 1H), 8.17 (s, 1H), 8.10 (s, 1H), 7.89 (m, 3H), 7.73 (m, 12H), 7.25 (m, 1H), 7.16 (m, 1H), 5.39-5.33 (d, 2H), 2.51 (s, 3H). **MALDI-TOF** (m/z): calculated for $[M+H]^+$: 445.53, found: 445.60.

Synthesis of compound 5



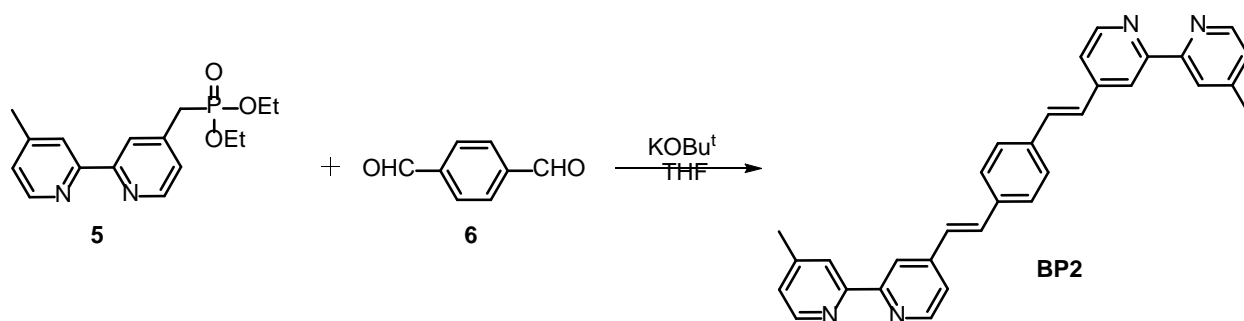
Compound **2** (3 g, 11.4 mmol) and triethylphosphite (20 ml) were dissolved in 100 mL CHCl_3 and refluxed at 80 °C for 24 h under nitrogen atmosphere. The solution was then cooled to room temperature followed by removal of solvent and the excess triethylphosphite under reduced pressure. An oily brown residue was obtained which was purified by column chromatography (silica gel, acetone as eluent). Finally, a clear oily liquid was obtained (3.1 g, 85 % yield). **^1H -NMR** (300 MHz, CDCl_3) δ (ppm): 8.62 (1H, d), 8.54 (1H, d), 8.32 (1H, s), 8.23 (1H, s), 7.32 (1H, d), 7.13 (1H, d), 4.10 (4H, m), 3.28 (2H, d), 2.44 (3H, s), 1.27-1.39 (6H, m). **MALDI-TOF** (m/z): calculated for $[M+H]^+$: 320.33, found: 320.97.

Synthesis of BP1



Compounds **3** (0.220 g, 1.12 mmol) and compound **4** (0.670 g, 1.28 mmol) were dissolved in EtOH (30 mL) and stirred under nitrogen at 0 °C for 20 min. A solution of 0.3 M NaOE/EtOH (4 mL) was added dropwise over a 5 min period, and the solution was allowed to warm to room temperature. After 5 h the volume was reduced to 15 mL by evaporation under reduced pressure and H₂O (10 mL) was added. The mixture was filtered to isolate the product as a white powder which was washed with 1:1 H₂O/EtOH and dried under vacuum and finally recrystallized from MeOH. **BP1** was obtained 0.175 g (43 % yield). **¹H-NMR** (300 MHz, CDCl₃) δ (ppm) 8.70 (2H, d), 8.60-8.58 (4H, m), 8.27 (2H, s), 7.42 (2H, s), 7.40 (2H, d), 7.17 (2H, d), 2.43 (6H, s). **MALDI-TOF** (*m/z*): calculated for [M+H]⁺: 364.45, found: 364.82. **IR**: 1590 cm⁻¹ (for C=C). **UV**: 288 nm (1 x 10⁻⁵ M, DCM).

Synthesis of BP2



Solid potassium tert-butoxide (0.45 g, 4 mmol) was added in one portion to a THF solution (50 mL) of compound **5** (0.704 mg, 2.2 mmol) and the terephthalaldehyde (0.134 g, 1 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 10 h at room temperature. The reaction mixture was subsequently quenched with water (25 mL), THF was removed under reduced pressure, and the aqueous residue was extracted with DCM. The collected organic layers were

washed with water (50 mL), dried over magnesium sulfate, and filtered. After evaporation of the solvent, the residue was recrystallized in DCM/Hexane (1:2) solvent mixture and the product was obtained as yellow crystalline solid (0.30 g, 65 % yield). **¹H-NMR** (300 MHz, CDCl₃) δ (ppm): 8.67 (2H, d), 8.60-8.54 (4H, m), 8.28 (2H, d), 7.60 (4H, m), 7.50-7.41 (4H, m), 7.20-7.15 (4H, m), 2.47 (6H, sb). **MALDI-TOF** (m/z): calculated for [M+H]⁺: 466.59, found: 466.57. **IR**: 1588 cm⁻¹ (for C=C). **UV**: 358 nm (1 x 10⁻⁵ M, DCM).

Synthesis of NBP1

A 10 mL DCM (1 × 10⁻⁴ M) solution of **BP1** was prepared by dissolving 0.35 mg of **BP1** into DCM, and the solution was filtrated before use. The solution was then poured into a vial with a diameter of 4 cm followed by addition of 10 mL pure water to cover the solution of **BP1** and wait for 2 h to form a water/oil interface. A 10 mL aqueous solution of Fe(BF₄)₂ 6H₂O (1 × 10⁻² M, filtrated prior to use) was then added slowly to the water phase. After 24 h, a blue film of the nanosheets was appeared at the interface. The aqueous layer was replaced with pure water, followed by the removal of both DCM and water. Ethanol and DCM mixture (1:1) was added to the **NBP1** film, which made a suspension as flakes. The product was then collected by filtration and dried in vacuo.

Synthesis of NBP2

Synthesis of **NBP2** was done by same procedure as like **NBP1**, except that **BP2** was used as ligand instead of **BP1** and the film was obtained in magenta color.

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Section S-4: SEM and TEM analysis

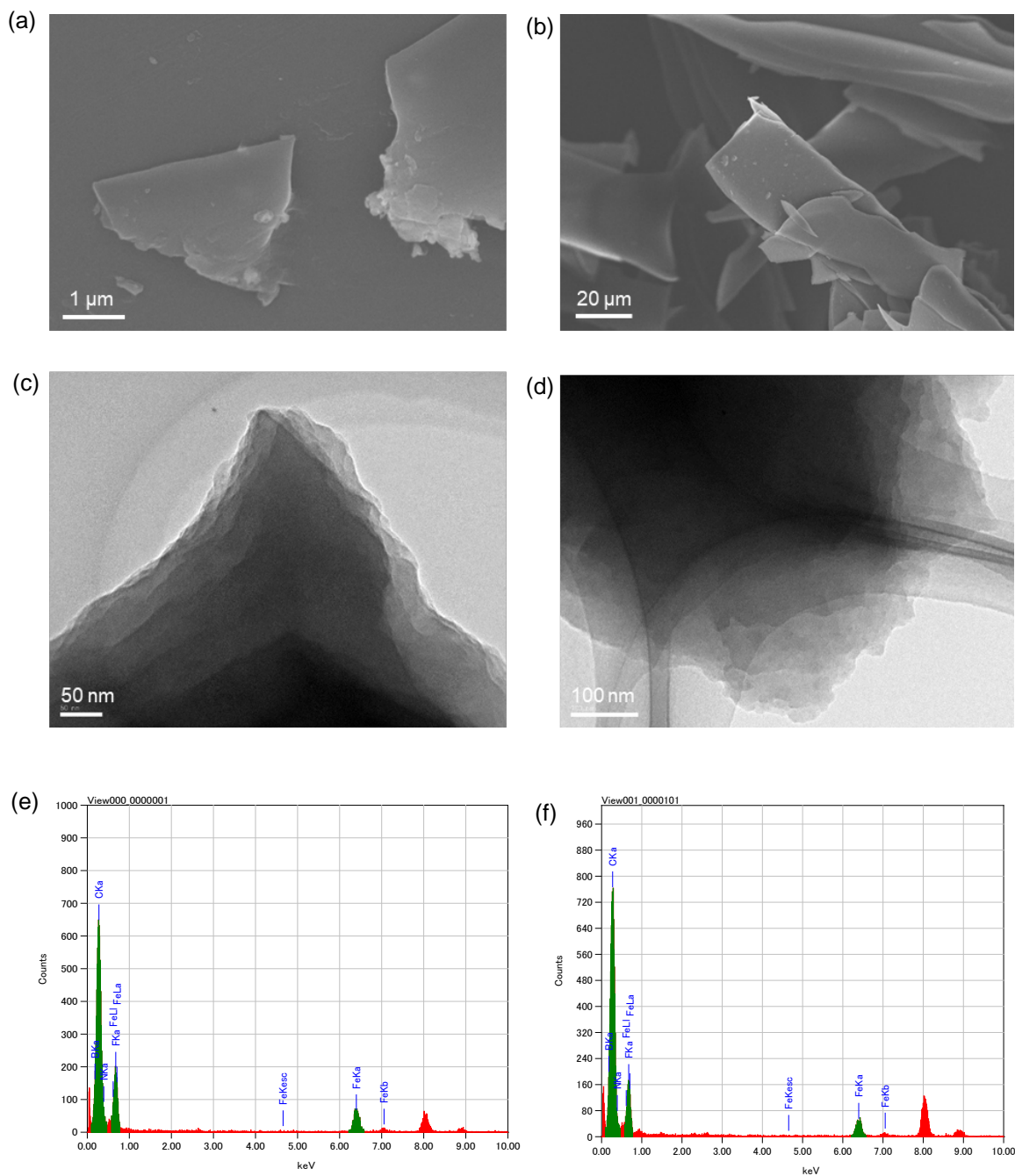
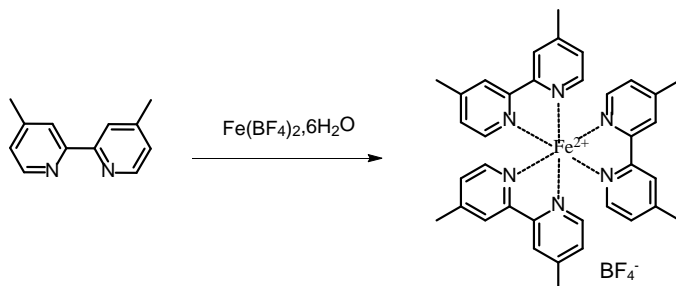


Figure S2. (a,b) Additional SEM images, (c,d) additional TEM images, and (e,f) EDX pattern of NBP1 and NBP2.

Section S-5: Synthesis and Optimized structure of MC

Synthesis of mononuclear complex (MC)



To a solution of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.168 g, 0.5 mmol) in MeOH, solution of 4,4'-Dimethyl-2,2'-dipyridine (0.276 g, 1.5 mmol) in MeOH was added slowly at 25°C under continuous stirring. After 30 min, the solution mixture was filtered off and mono complex was grown from the solution by slow evaporation at room temperature. **The elemental analysis (%)** calcd.: C (53.47), H (4.80), N (10.39); found: C (53.23), H (5.05), N (10.64). **IR:** 1618 cm^{-1} (for C=C), 1056 cm^{-1} (for counteranion BF_4^-). **Raman:** 1023 cm^{-1} (ring-breathing), 1484 cm^{-1} (C=N stretching), and 1548, 1613 cm^{-1} (C=C stretching). **XPS:** atomic ratio of N/Fe/B/F calcd: 6/1/1/4, found: 6/1/1/4.1.

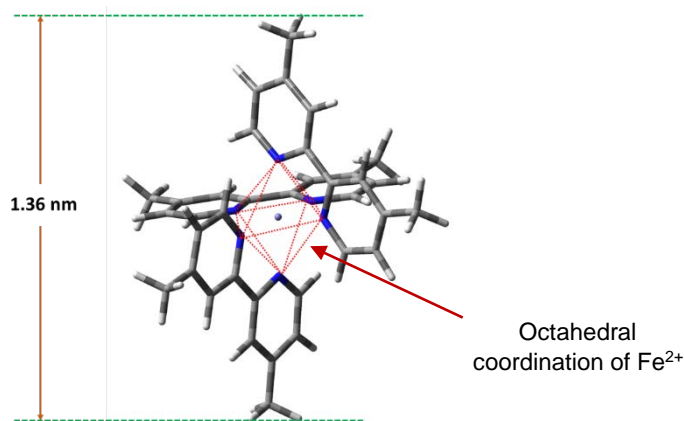


Figure S3. Optimized structure of MC obtained by DFT calculation.

Section S-6: XPS analysis

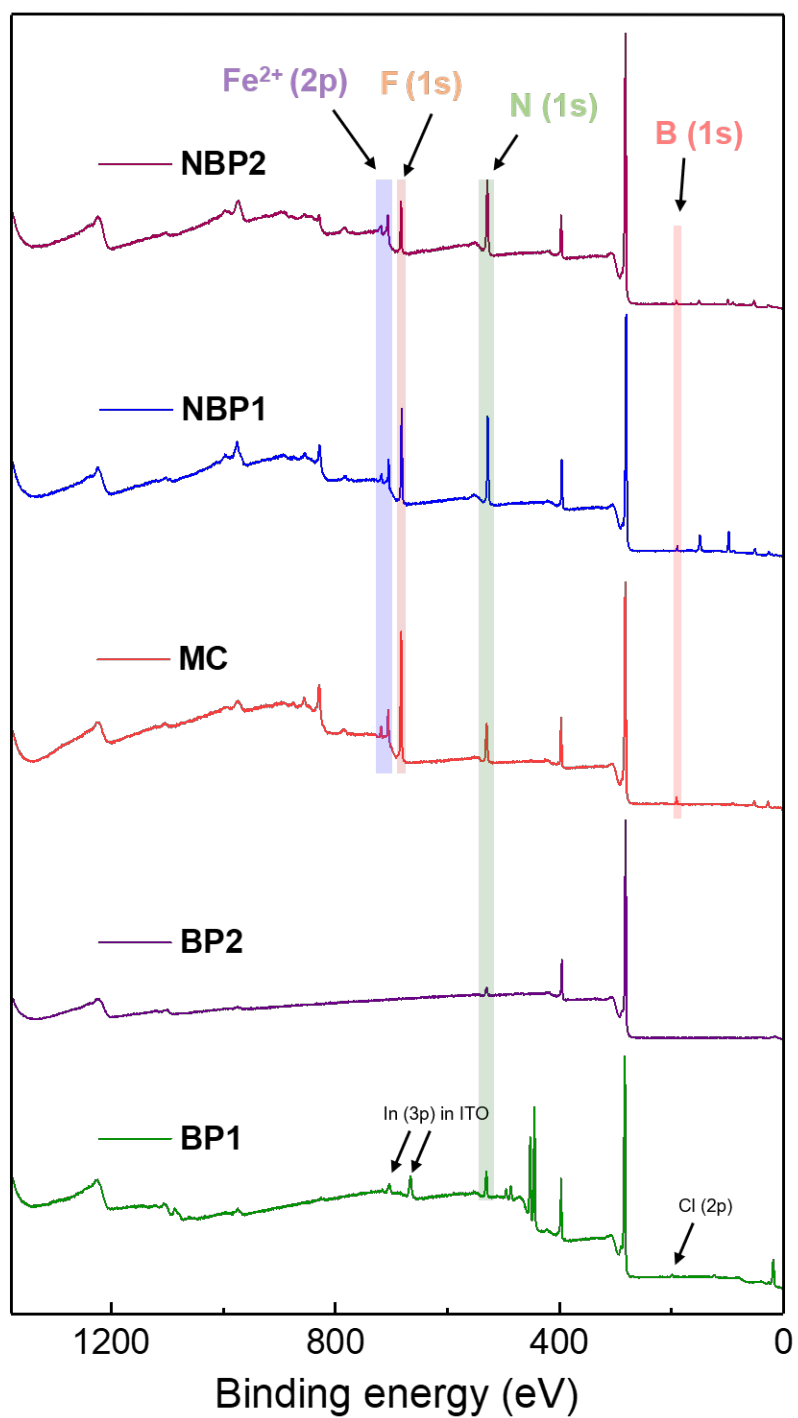


Figure S4. XP survey spectra of **BP1**, **BP2**, **MC**, **NBP1**, and **NBP2**.

Section S-7: IR, Raman, PXRD, TGA, UV-vis and CV study

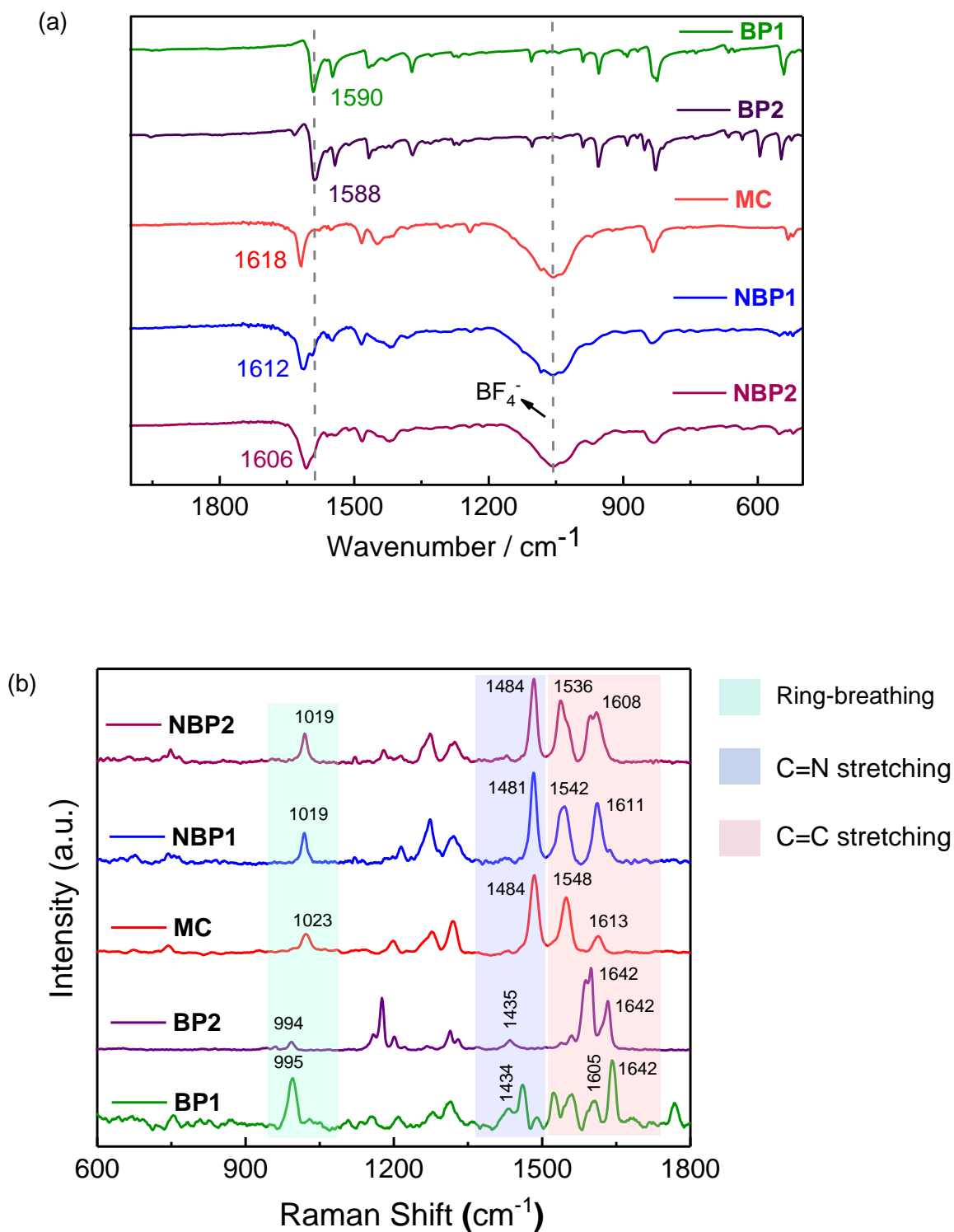


Figure S5. (a) IR and (b) Raman spectra of **BP1**, **BP2**, **MC**, **NBP1**, and **NBP2**.

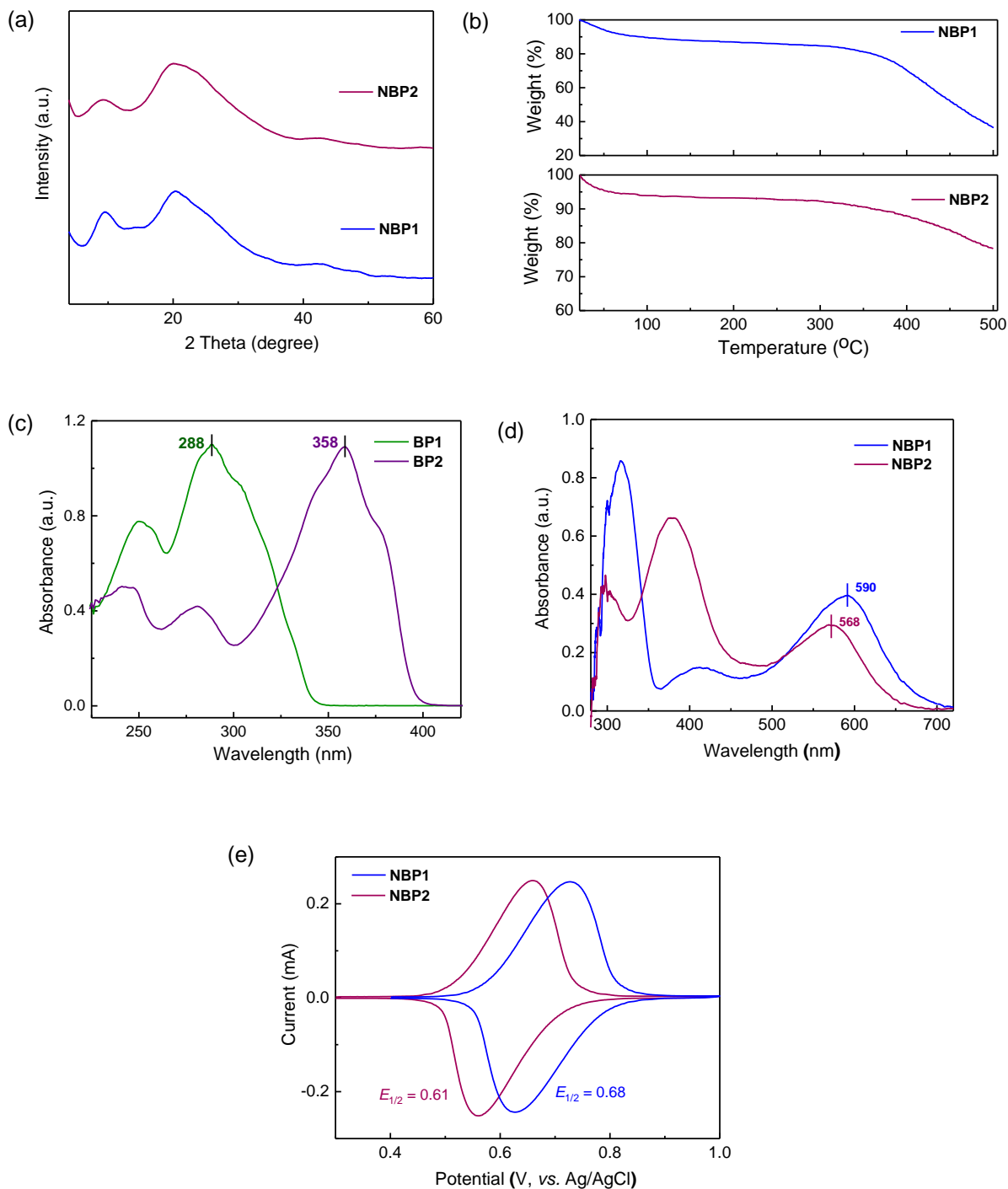


Figure S6. (a) Powder X-ray diffraction (PXRD) patterns of the CONASHs, (b) TGA analysis under N_2 atmosphere show the high thermal stability (up to 350 °C) of the CONASHs, (c) UV-vis spectra of **BP1**, **BP2**, (in DCM; 5×10^{-6} M). (d) UV-vis spectra, and (e) CV spectra (electrolyte: 0.1 M $LiClO_4/CH_3CN$, scan rate 50 mV/s) of **NBP1** and **NBP2** on ITO.

Section S-8: Synthesis of monolayer and its height analysis by AFM

Synthesis of monolayer of NBP1 at air/liquid interface

The monolayer film of **NBP1** was prepared using a USI-3-777C3 Langmuir-Blodgett system (USI Co., Fukuoka). The trough contains the 1 L subphase (water containing Fe(II) salt) and has a working area of $544 \times 150 = 8.16 \times 10^4 \text{ mm}^2$. The ligand **BP1** was dissolved in DCM ($2.7 \times 10^{-3} \text{ M}$) and spread (50 μL) on the water containing Fe^{2+} salt ($1 \times 10^{-3} \text{ M}$). After prompt vaporization of DCM, the film was compressed at the rate of 0.2 mm s^{-1} to the predetermined surface pressures at $20.0 \pm 0.2 \text{ }^\circ\text{C}$. The film at the air-water interface was horizontally transferred onto a silicon wafer.

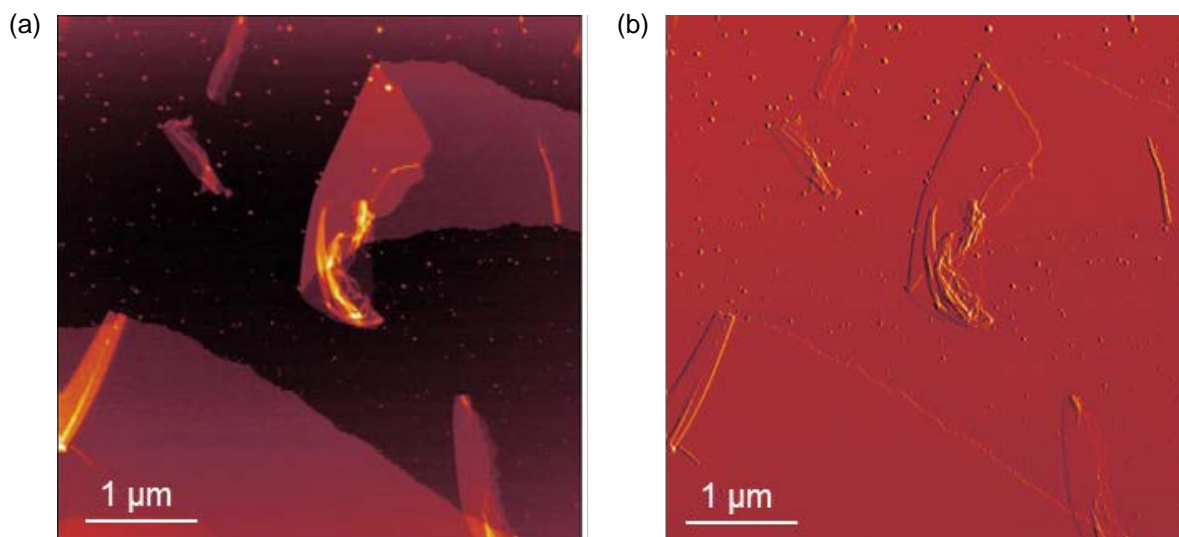


Figure S7. AFM image of monolayer of **NBP1**; topography (a), phase (b).

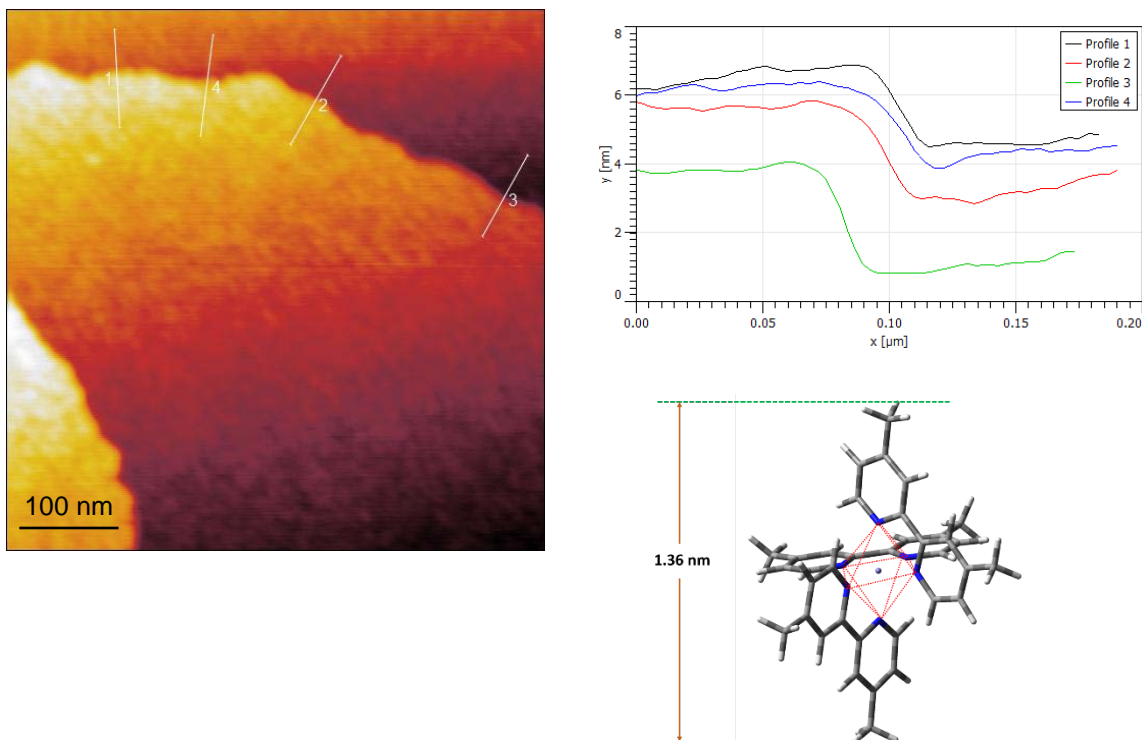


Figure S8. Measurement of heights at different positions of monolayer.

The molecular length of mononuclear complex (**MC**) is 1.36 nm calculated from the optimized structure by density functional theory (DFT). The thickness of the monolayer measured at four positions as mentioned above which revealed 2 nm, 2nm, 2.5 nm, 3 nm. So, taking average of these four measurements give the approximate height of ~2.4 nm. This height is quite reasonable with the molecular length of **MC** if counter anions and/or water layer are taken in to consideration.⁸⁻⁹

Section S-9: Height analysis of multilayer NBP1 by AFM

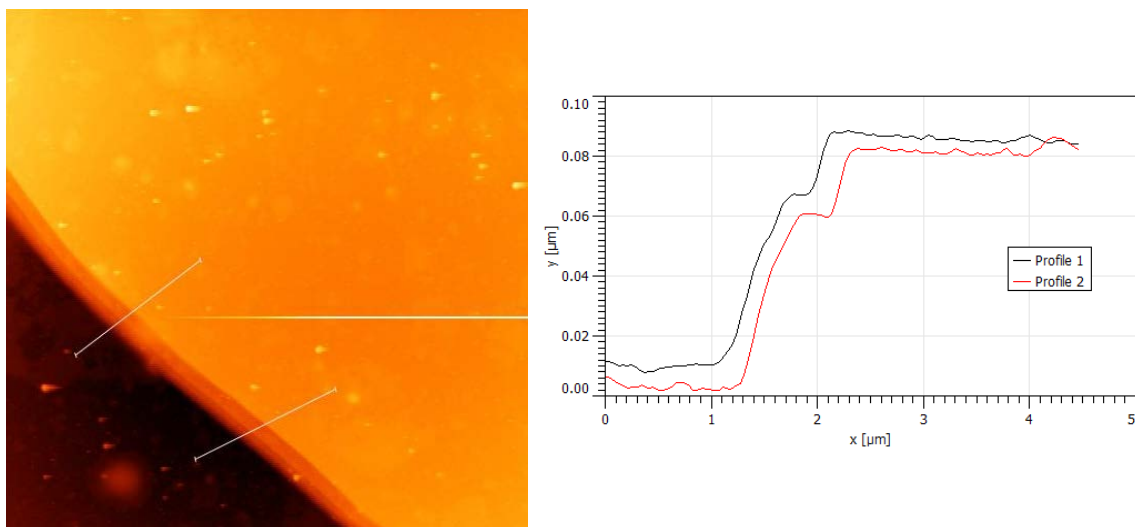


Figure S9. AFM image of **NBP1** obtained after 24 h using 5 mM $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ solution with height measurement from cross section analysis.

Section S-10: Electrochromic analysis

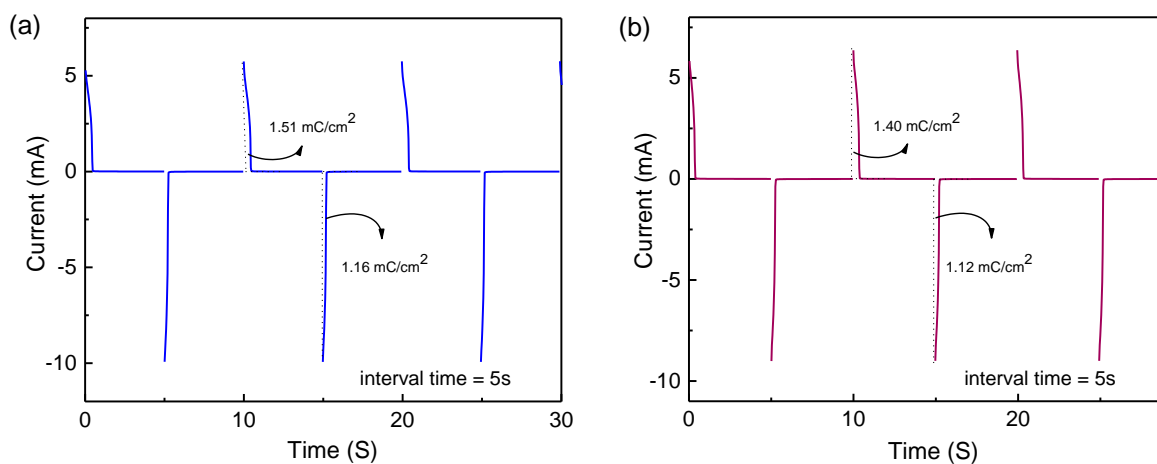


Figure S10. Charge/discharge curve of **NBP1** (a), and **NBP2** (b) thin film on ITO (electrolyte: 0.1 M LiClO₄/CH₃CN, scan rate 50 mV/s), dimension: 1 cm × 1 cm.

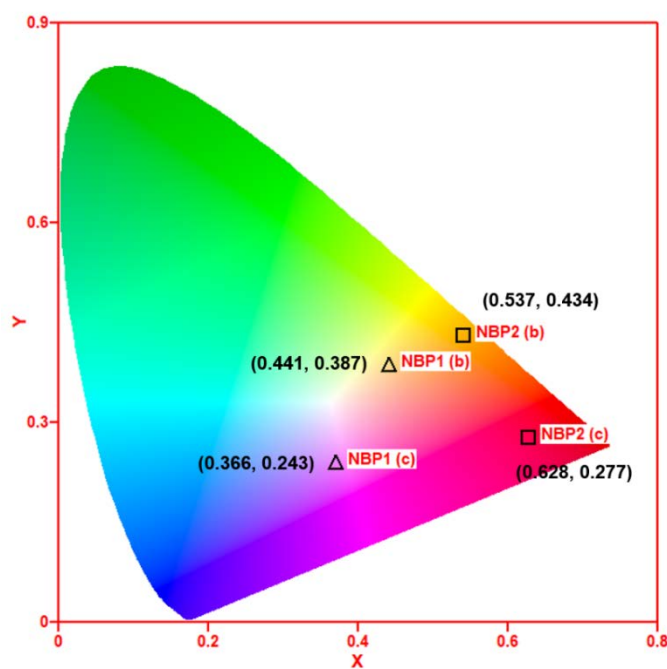


Figure S11. CIE chromaticity diagram with chromaticity coordinates for the electrochromic color of the **NBP1** and **NBP2** based electrochromic devices before (denoted by 'c') and after oxidation (denoted by 'b').

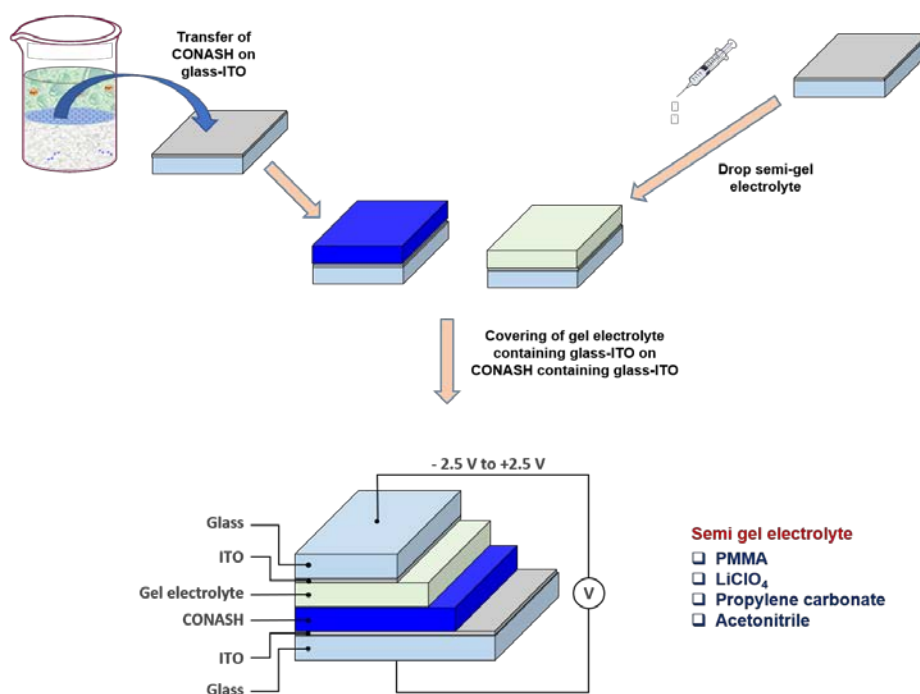


Figure S12. Schematic presentation for fabrication of solid-state electrochromic device.

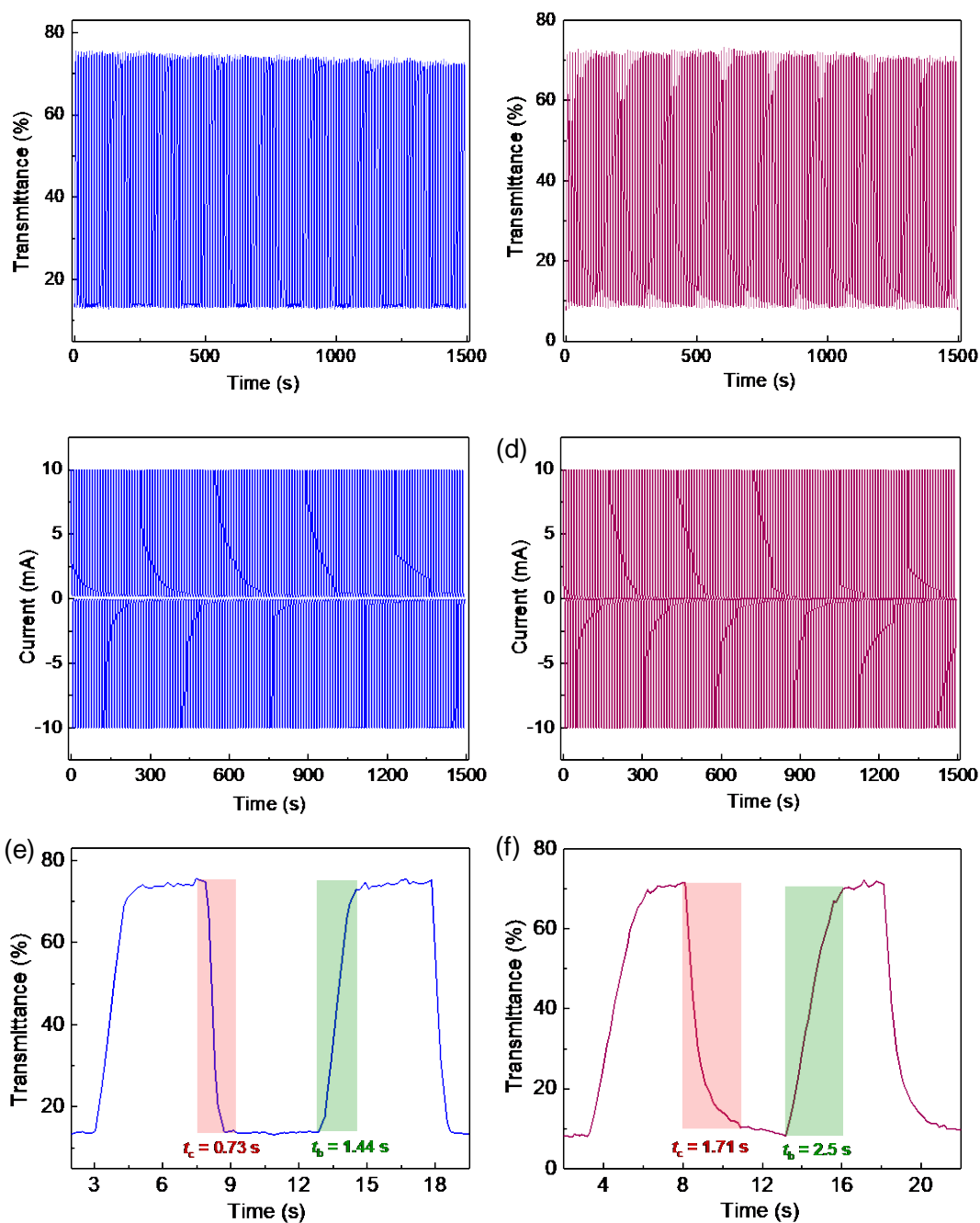


Figure S13. (a,b) SEC switching stability (ΔT vs time) of the devices up to 300 cycles with a pulse width 5 s, (c,d) Flow of current as a function of time during SEC switching stability measurement, and (e,f) Response time for coloration (t_c), bleaching (t_b) of devices based of **NBP1** and **NBP2**, respectively. In each case, the applied voltage was switched between +2.5 V and -2.5 V. Dimension of the devices were 2 cm \times 1.5 cm

Section S-11: Comparison of electrochromic properties

Table ST1: Comparison of electrochromic properties of our material with previously reported different types of electrochromic materials.

Type of material	Molecular unit / framework / binding ligand	Optical contrast / transmittance change (ΔT , %)	Coloration efficiency (η , cm ² /C)	Solid-state device fabrication	Durability of solid-state device	References
Metallo-supramolecular Polymers (1D or 3D)	Terpyridine based ligands	41.6 (for 1D polymer) 50.7 (for 3D polymer)	263.8 (for 1D polymer) 383.4 (for 3D polymer)	Not reported	Not reported	<i>ACS Appl. Mater. Interfaces</i> 2014 , 6 (12), 9118-9125
Inorganic oxide	WO ₃	97.7	118.3	Not reported	Not reported	<i>Chem. Sci.</i> 2016 , 7, 1373-1382
Metal-organic molecular assemblies	Polypyridyl complexes	65 (up to)	474 (up to)	Shown	for at least 75 cycles	<i>J. Am. Chem. Soc.</i> 2017 , 139, 11471-11481
Plasmonics	Au and Al metallic nanoslit arrays on electrochromic polymer	90	Not reported	Not reported	Not reported	<i>Nat. Commun.</i> 2016 , 7, 10479
π -conjugated polymer	Dioxythiophene	72	375	Not reported	Not reported	<i>Chem. Mater.</i> 2002 , 14, (9), 3964-3970
Electropolymerized film of metal-complex	Cyclometalated ruthenium complex	40	250	Not reported	Not reported	<i>J. Am. Chem. Soc.</i> 2011 , 133, 20720-20723
CONASHs	Terpyridine	Not reported	Not reported	Shown	Not reported	<i>J. Am. Chem. Soc.</i> 2015 , 137, 4681-4689
CONASHs	Bis(2,2'-bipyridine) based ligand	62 (up to)	431 (up to)	Shown	For at least 300 cycles	This work

Section S-12: References

References

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