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## Supporting Information

# Electron-Accepting Carborane Viologen and Iron based-Supramolecular Polymers for Electrochromism and Enhanced Photocatalytic Hydrogen Evolution

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### Table of Contents

Table of Contents .....	1
Experimental Procedures .....	2
1. Materials and instrumentation.....	2
2. Synthetic procedures.....	3
3. Single-crystal X-ray structure determination .....	7
4. XRD patterns.....	8
5. SEM-EDX.....	8
6. The cyclic voltammogram.....	10
7. Electrochromism.....	12
8. H <sub>2</sub> normalized curve .....	15
9. Hydrogen generation under xenon lamp.....	16
10. Computed UV-vis spectra.....	18
11. DFT Calculations (PBE0/6-31G*) .....	21
12. <sup>1</sup> H, <sup>13</sup> C, <sup>11</sup> B <sup>19</sup> F NMR spectra .....	22
13. The HRMS spectra .....	30
Reference.....	33
Author Contributions.....	33

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## Experimental Procedures

### 1. Materials and instrumentation

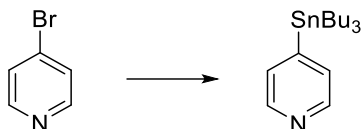
**General.** All reactions were performed using standard Schlenk and glovebox (Vigor) techniques under argon atmosphere. toluene, THF, DMF were distilled from sodium/benzophenone prior to use. Decaborane (99%), Bis(4-bromophenyl)acetylene (98.5%), 4-Bromopyridine (98 %), *N*-Bromosuccinimide (98 %), 4-Methylbenzaldehyde (99 %), Tributylstannium chloride (98 %), 4,4'-Bipyridine (99 %), Ferrous acetate (99 %) were purchased from Energy Chemical Inc. 4-(tetrabutyl-stannyl)pyridine<sup>[1]</sup> and 4'-(4-(bromomethyl)phenyl)-2,2':6',2''-terpyridine.<sup>[2]</sup> were prepared according to literature procedures, If no other special indicated, other reagents and solvents were used as commercially available without further purification. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel.

NMR spectra were measured on a Bruker Avance-400 spectrometer in the solvents indicated; chemical shifts are reported in units (ppm) by assigning TMS resonance in the <sup>1</sup>H spectrum as 7.26 ppm, CDCl<sub>3</sub>, 2.50 ppm, DMSO-d<sub>6</sub> or 3.31 ppm, CD<sub>3</sub>OD resonance in the <sup>13</sup>C spectrum as 77.0 ppm or 35.0 ppm. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). UV-vis measurements were performed using DH-2000-BAL Scan spectrophotometer. The cyclic voltammetry (CV) were measured using CHI660E, with a polished gold electrode as the working electrode, a Pt-net as counter electrode, and an Ag wire as reference electrode, using ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) as internal standard (the redox potentials presented in the text are half-wave potential). High-resolution mass spectra (HRMS) were collected on a Bruker maXisUHR-TOF mass spectrometer in an ESI positive mode. Analytical gas chromatography (GC) for gas sample were carried out on a agilent (8860, N<sub>2</sub> carrier gas). Field emission SEM-EDX was recorded on Quanta FEG 250, FEI. EPR was measured using a Bruker EMX PLUS6/1 instrument at room temperature in dry degassed DMF.

All the computational calculations reported in this work were performed using the Gaussian 09 code. To simulate the experimental UV-Vis in *N,N*-Dimethylformamide (DMF), the Polarizable Continuum Model (PCM)<sup>[3]</sup> as a self-consistent reaction field (SCRF) was used for the calculation of equilibrium geometries, vibrational frequencies and excited state calculations. The geometries for the ground state of these compounds in the DMF solution were optimized at TD-PBE0/6-31G\* //PBE0/6-31G\*<sup>[4]</sup> basis and the keyword "opt=tight" was used. All isosurface values are ±0.03.

## 2. Synthetic procedures

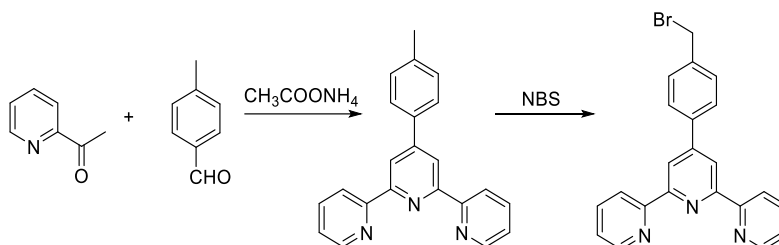
### 2.1 Synthesis of 4-(tributylstannyl)pyridine.



Following a reported procedure, to a solution of 4-Bromopyridine (3.16 g, 20 mmol) in THF (40 mL) was added dropwise a *n*-BuLi (1.60 M in hexane, 13.75 mL, 22 mmol) in THF (40 mL) at -78 °C under Ar atmosphere. After stirring for 2 h, Tributylstannium chloride (6.5 mL, 24 mmol) was added, and the mixture was additionally stirred at this temperature for 1 h. Then the mixture was warmed to room temperature and stirred overnight. The emulsion was extracted with a solution of ethyl acetate (3 x 100 mL), The organic phase was washed with cold water, dried over MgSO<sub>4</sub> and evaporated under reduced pressure to afford **4-(tributylstannyl)pyridine** (7.4 g, 87%). without further purification.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.47 (d, *J* = 4.4 Hz, 2H), 7.36 (d, *J* = 4.4 Hz, 2H), 1.50-1.58 (m, 6H), 1.30-1.36 (m, 6H), 1.08-1.12 (m, 6H), 0.87-0.91 (m, 9H). The <sup>1</sup>H NMR data are consistent with the reported ones.<sup>[1]</sup>

### 2.2 Synthesis of 4'-(4-(bromomethyl)phenyl)-2,2':6',2''-terpyridine.



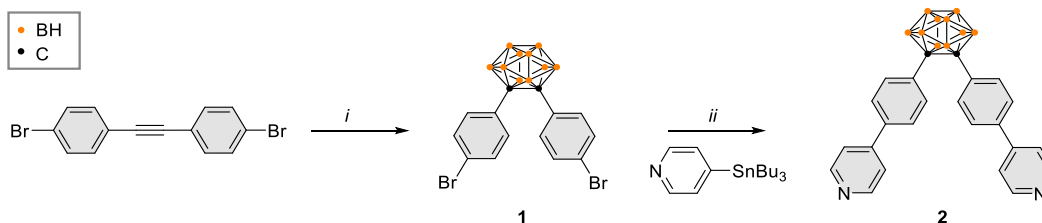
Following a reported procedure,

1) 2-Acetylpyridine (2.42 g, 20 mmol) and *p*-tolualdehyde (1.2 g, 10 mmol), CH<sub>3</sub>COONH<sub>4</sub> (770 mg, 10 mmol), K<sub>2</sub>CO<sub>3</sub> (2.76 g, 20 mmol), were dissolved in 60 mL of DMF and under Ar atmosphere. The mixture was stirred at 60 °C for 1 d. After cooling to room temperature, the emulsion was extracted with a solution of ethyl acetate (3 x 100 mL), The organic phase was washed with cold water, dried over MgSO<sub>4</sub> and evaporated under reduced pressure to afford **4'-(*p*-tolyl)-2,2':6',2''-terpyridine** (3.13 g, 97%). without further purification.

2) 4'-(*p*-tolyl)-2,2':6',2''-terpyridine (2.5 g, 8 mmol) and NBS (1.57 g, 8.8 mmol), AIBN (26 mg, 0.16 mmol) were dissolved in 40 mL of CCl<sub>4</sub> and under Ar atmosphere. The mixture was refluxed for 6 h. After cooling to room temperature, the solvent was removed and violet solid washed with little of DCM and EtOH via vacuum filtration. Recrystallization in CCl<sub>4</sub> to obtain **4'-(4-(bromomethyl)phenyl)-2,2':6',2''-terpyridine** with the yields (2.44 g, 76 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.71 (d, *J* = 4.0 Hz, 4H), 8.65 (d, *J* = 8.0 Hz, 2H), 7.85-7.90 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.33-7.37 (m, 2H), 4.56 (s, 2H). The <sup>1</sup>H NMR data are consistent with the reported ones.<sup>[2]</sup>

### 2.3 Preparation of 2.



Decaborane (1.22 g, 10 mmol) was dissolved in 80 mL of toluene and *N,N*-dimethylaniline (1.75 mL, 13.8 mmol) under Ar atmosphere. After the mixture was stirred at room temperature for 1 h. Bis(4-bromophenyl)acetylene (3 g, 9 mmol) was added, and the mixture was additionally refluxed for 2 d. Then cooling to room temperature, insoluble products were removed by filtration, and the solvent was

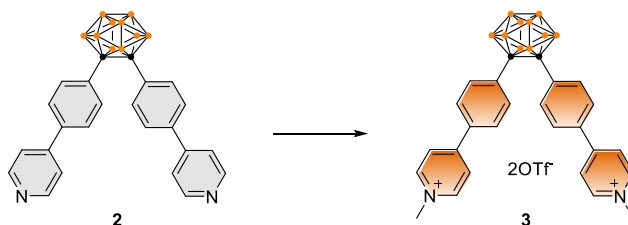
evaporated. The residue was purified by column chromatography on a silica gel (hexane/DCM v/v = 10:1). After evaporation of solvents, recrystallization from DCM/hexane afforded the desired compound **1** as a white powder (3.1 g, 76%).

The date of **1**. melting point: 199-201 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.26-7.32 (m, 8H), 3.05-2.07 (cage 10H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 132.04, 131.75, 129.58, 125.40, 84.12. <sup>11</sup>B {<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>): δ -3.03 (2B), -11.14-11.56 (8B). HRMS calcd for C<sub>14</sub>H<sub>18</sub>B<sub>10</sub>Br<sub>2</sub> [M+H]<sup>+</sup> 455.0779; found: 455.0783.

**1** (1.81 mg, 4 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (231 mg, 0.2 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>) (140 mg, 0.02 mmol), PPh<sub>3</sub> (210 mg, 0.8 mmol), were dissolved in 60 mL of toluene and under Ar atmosphere. Then 4-(tetrabutyl-stannyl)pyridine (5.1 g, 12 mmol) were added. The mixture was refluxed for 2 d. Then cooling to room temperature, insoluble products were removed by filtration, and the solvent was evaporated. The residue was purified by column chromatography on a silica gel (hexane/DCM v/v = 4:1 then DCM). After evaporation of solvents, recrystallization from DCM/hexane afforded the desired compound **2** as a white powder (0.83 g, 46%).

The date of **2**. melting point: 94-96 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.62 (d, *J* = 5.6 Hz, 4H), 7.58 (d, *J* = 8.4 Hz, 4H), 7.44 (d, *J* = 8.4 Hz, 4H), 7.39 (d, *J* = 5.6 Hz, 4H), 2.21-2.96 (cage 10H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.19, 146.52, 139.79, 131.49, 131.40, 126.92, 121.42, 84.49. <sup>11</sup>B {<sup>1</sup>H} NMR (128 MHz, CDCl<sub>3</sub>): δ -0.66 (6B), -7.22(-7.38) (4B). HRMS calcd for C<sub>24</sub>H<sub>26</sub>B<sub>10</sub>N<sub>2</sub> [M+H]<sup>+</sup> 453.3100; found: 453.3106.

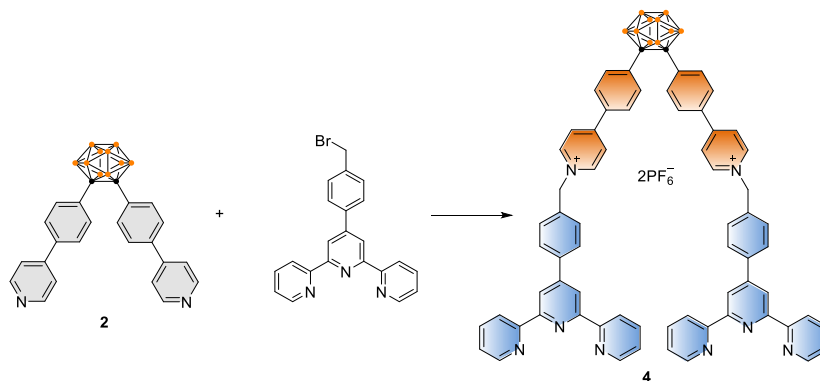
#### 2.4 Preparation of carborane viologen **3**.



**2** (0.25 mmol) was dissolved in dried and degassed DCM (10 mL), while stirring, Trifluoromethanesulfonate (85 μL, 0.75 mmol) was added by dropwith. After 24h later, the precipitate was isolated via vacuum filtration and washed with DCM (10 mL) for at least 3 times. The precipitate was collected and dried under high vacuum to obtain **3** with the yields (136 mg, 70 %).

The date of **3**. melting point: 238-240 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 9.26 (d, *J* = 6.8 Hz, 4H), 8.70 (d, *J* = 4.4 Hz, 4H), 8.59 (d, *J* = 10.8 Hz, 8H), 8.48 (d, *J* = 6.8 Hz, 4H), 7.94-8.03 (m, 12H), 7.85 (d, *J* = 8.4 Hz, 4H), 7.69 (d, *J* = 8.4 Hz, 4H), 7.50-7.53 (m, 4H), 5.91 (s, 4H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ 155.74, 154.97, 154.83, 149.43, 149.10, 146.78, 145.13, 138.66, 138.31, 136.09, 132.97, 130.58, 129.98, 128.21, 127.26, 125.18, 124.65, 121.63, 118.60, 62.34. <sup>11</sup>B {<sup>1</sup>H} NMR (128 MHz, DMSO-d<sub>6</sub>): δ -3.31 (2B), -10.44(-12.41) (8B). <sup>19</sup>F NMR (376 MHz, DMSO-d<sub>6</sub>): δ: 78.80. HRMS calcd for C<sub>26</sub>H<sub>32</sub>B<sub>10</sub>N<sub>2</sub><sup>2+</sup> [M<sup>2+</sup>] 482.3496; found: 482.3489.

#### 2.5 Preparation of carborane viologen ligand **4**.

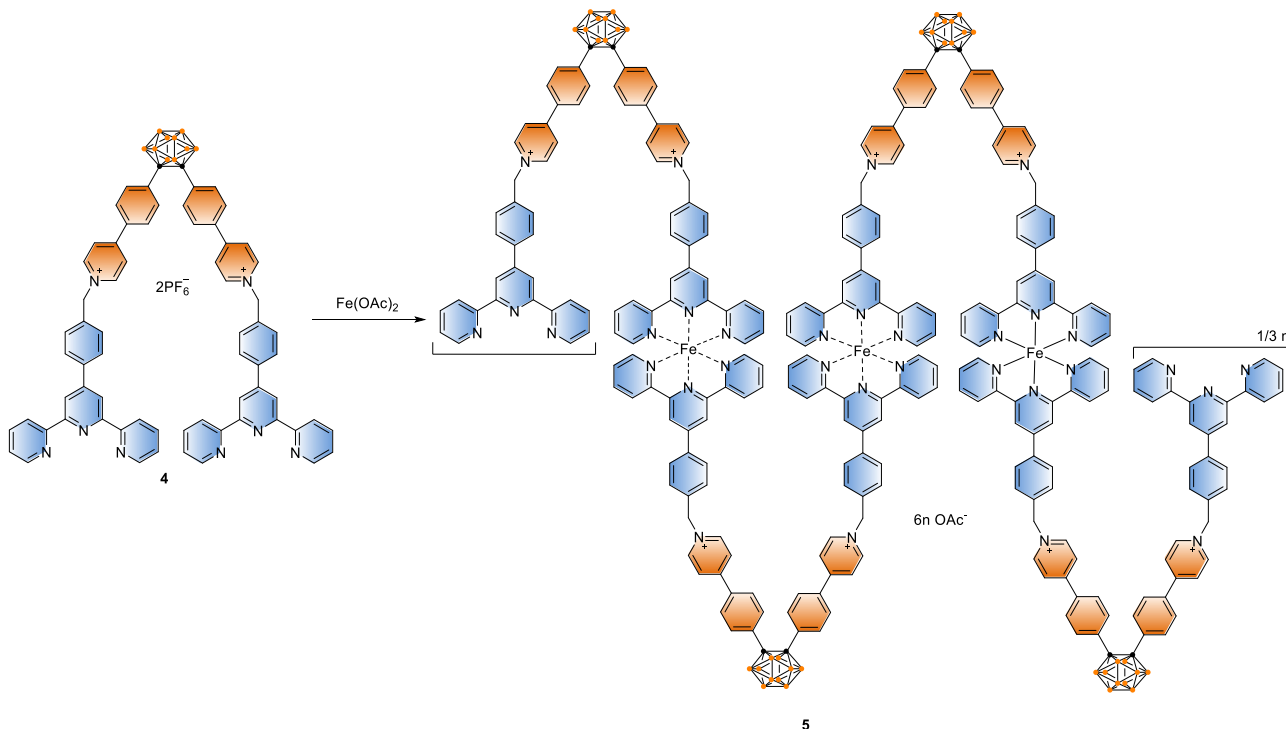


**2** (0.25 mmol) and 4'-(4-(bromomethyl)phenyl)-2,2':6',2''-terpyridine (220.6 mg, 0.55 mmol) were dissolved in dried and degassed DMF (30 mL) and heated to 60 °C for 3 d while stirring. The precipitate was isolated via vacuum filtration and washed with dichloromethane (3 x30 mL) for at least 3 times. The precipitate was collected and dried under high vacuum to obtain **4** with the yields (221 mg, 65 %).

The date of **4**. melting point: 223-225 °C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 8.97 (d, *J* = 8.0 Hz, 4H), 8.41 (d, *J* = 8.0 Hz, 4H), 7.95 (d, *J* = 8.0 Hz, 4H), 7.86 (d, *J* = 8.0 Hz, 4H), 7.94-8.03 (m, 4H), 4.30 (s, 6H). <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ 154.07, 146.50, 146.19, 145.77, 132.93,

132.31, 130.69, 128.93, 127.08, 124.98, 123.81, 47.31.  $^{11}\text{B}$   $\{^1\text{H}\}$  NMR (128 MHz, DMSO- $d_6$ ):  $\delta$  -6.12-7.24 (3B), -13.05-16.98 (7B). HRMS calcd for  $\text{C}_{66}\text{H}_{58}\text{B}_{10}\text{N}_8^{2+}$  [ $\text{M}^{2+}$ ] 1072.5715; found: 1072.5726.

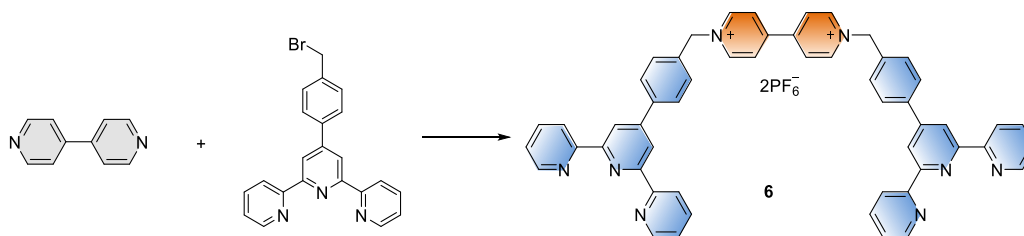
## 2.6 Preparation of carborane viologen-based metallo-supramolecular polymer 5.



**4** (0.25 mmol) and Ferrous acetate (48.5 mg, 0.25 mmol) were dissolved in dried and degassed Acetic Acid (30 mL) and refluxed for 2 d while stirring. The solvent was removed and violet solid washed with DCM and little of DMF via vacuum filtration. The precipitate was collected and dried under high vacuum to obtain **5** with the yields (377.3 mg, 96 %).

The date of **5**.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  9.47 (m, 4H), 9.13 (d,  $J = 8.0$  Hz, 4H), 8.83 (m, 6H), 8.43-8.56 (m, 8H), 7.91-7.99 (m, 8H), 7.49 (d,  $J = 8.0$  Hz, 2H), 7.18-7.29 (m, 8H), 7.02 (s, 4H), 6.04 (s, 4H).

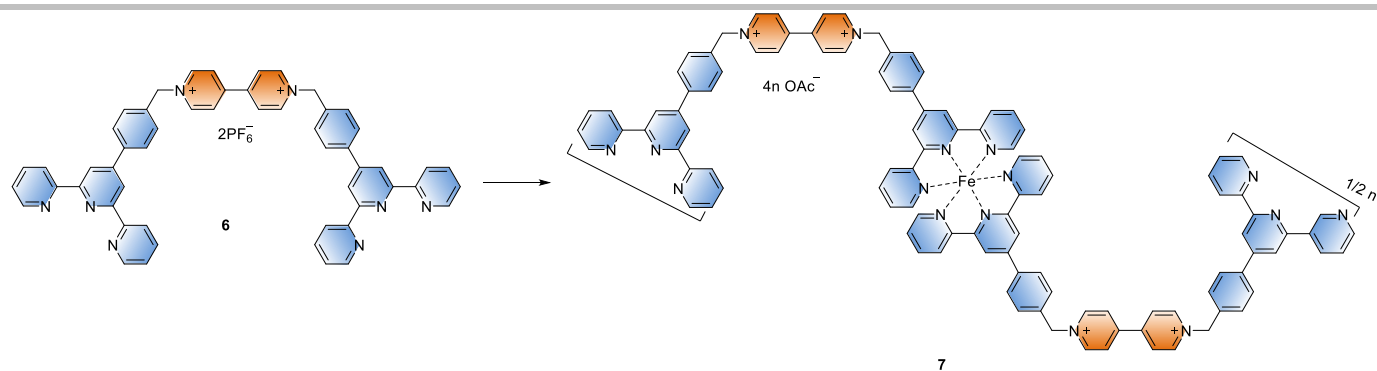
## 2.7 Preparation of dipyridyl-viologen ligand 6.



4,4'-Bipyridine (0.25 mmol) and 4-(4-(bromomethyl)phenyl)-2,2':6,2''-terpyridine (220.6 mg, 0.55 mmol) were dissolved in dried and degassed DMF (20 mL) and heated to 60  $^\circ\text{C}$  for 3 d while stirring. The precipitate was isolated via vacuum filtration and washed with dichloromethane (3  $\times$  30 mL) for at least 3 times. The precipitate was collected and dried under high vacuum to obtain **6** with the yields (193 mg, 71 %).

The date of **6**. melting point: 272-274  $^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  9.26 (d,  $J = 6.8$  Hz, 4H), 8.70 (d,  $J = 4.4$  Hz, 4H), 8.59 (d,  $J = 10.8$  Hz, 8H), 8.48 (d,  $J = 6.8$  Hz, 4H), 7.94-8.03 (m, 12H), 7.85 (d,  $J = 8.4$  Hz, 4H), 7.69 (d,  $J = 8.4$  Hz, 4H), 7.50-7.53 (m, 4H), 5.91 (s, 4H).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  155.58, 154.49, 149.82, 149.38, 149.26, 146.30, 138.93, 135.75, 130.54, 128.48, 127.77, 125.49, 122.00, 119.05, 63.61. HRMS calcd for  $\text{C}_{54}\text{H}_{40}\text{N}_8^{2+}$  [ $\text{M}^{2+}$ ] 800.3370; found: 800.3377.

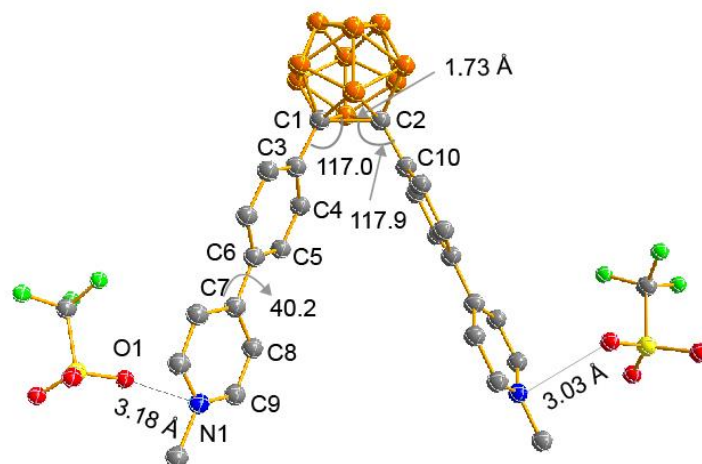
## 2.8 Preparation of dipyridyl-viologen-based metallo-supramolecular polymer 7.



**6** (0.25 mmol) and Ferrous acetate (48.5 mg, 0.25 mmol) were dissolved in dried and degassed Acetic Acid (30 mL) and refluxed for 2 d while stirring. The solvent was removed and violet solid washed with DCM and little of DMF via vacuum filtration. The precipitate was collected and dried under high vacuum to obtain **7** with the yields (272.5 mg, 98 %).

The data of **7**.  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  9.46-9.53 (m, 4H), 9.35 (d,  $J = 4.0$  Hz, 2H), 8.84-8.87 (m, 6H), 8.56-8.65 (m, 6H), 8.40 (d,  $J = 8.0$  Hz, 2H), 8.32 (d,  $J = 8.0$  Hz, 2H), 7.98-8.04 (m, 6H), 7.29-7.31 (m, 4H), 7.17 (d,  $J = 8.0$  Hz, 4H), 6.14 (s, 4H).

### 3. Single-crystal X-ray structure determination



**Figure S1.** Molecular Structure of **3** with thermal ellipsoids presented at room temperature. Selected Bond lengths [Å] and angles [deg]: S(1)-O(1) 1.435(3), S(2)-C(26) 1.809(5), N(1)-C(11) 1.343(5), C(7)-C(6) 1.483(5), C(7)-C(12) 1.390(5), C(2)-B(02F) 1.724(5), C(3)-C(1) 1.506(5), C(9)-H(9) 0.9300, O(1)-S(1)-O(3) 114.72(16), O(1)-S(1)-O(2) 116.13(17), O(4)-S(2)-O(6) 114.74(17), C(9)-N(1)-C(11) 120.1(3), C(12)-C(7)-C(8) 116.1(3), C(8)-C(7)-C(6) 121.5(3), C(15)-C(10)-C(19) 118.2(3), C(3)-C(4)-H(4) 119.3, C(4)-C(5)-H(5) 119.7. (CCDC 2018519)

**Table S1.** Crystal data and structure refinement for **3**.

Empirical formula	C <sub>28</sub> H <sub>32</sub> B <sub>10</sub> F <sub>6</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>
Formula weight	780.25
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 1 21/c 1
Unit cell dimensions	a = 14.174(3) Å    alpha = 90 deg. b = 36.094(6) Å    beta = 101.361(2) deg. c = 15.467(3) Å    gamma = 90 deg.
Volume	7757(2) Å <sup>3</sup>
Z, Calculated density	4, 1.372 Mg/m <sup>3</sup>
Absorption coefficient	0.211 mm <sup>-1</sup>
F(000)	3284
Crystal size	0.28 x 0.0.21 x 0.18 mm <sup>3</sup>
Theta range for data collection	1.457 to 25.579 deg.
Limiting indices	-17<=h<=17, -43<=k<=43, -18<=l<=18
Reflections collected / unique	76850 / 14486 [R(int) = 0.0709]
Completeness to theta = 25.242	100.0 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	14486 / 26 / 1005
Goodness-of-fit on F <sup>2</sup>	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1428
R indices (all data)	R1 = 0.1064, wR2 = 0.1678
Extinction coefficient	n/a
Largest diff. peak and hole	1.044 and -0.818 e.Å <sup>-3</sup>

## 4. XRD patterns

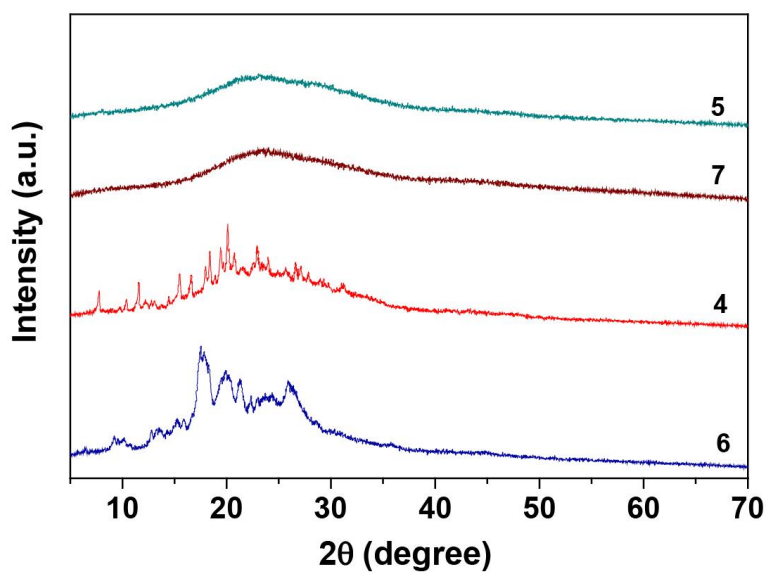


Figure S2. XRD patterns of 4 - 7.

## 5. SEM-EDX

Table S2. The SEM-EDX dates of 5

Element	wt (%)	at (%)
B (K)	7.47	8.58
C (K)	52.53	70.56
N (K)	7.92	9.12
O (K)	9.38	6.36
Fe (L)	22.70	5.38
Total	100	100

Table S3 The SEM-EDX dates of 7

Element	Weight (%)	Atomic (%)
C (K)	50.01	69.41
N (K)	8.92	10.61
O (K)	10.38	10.82
Fe (L)	30.70	9.16
Total	100	100



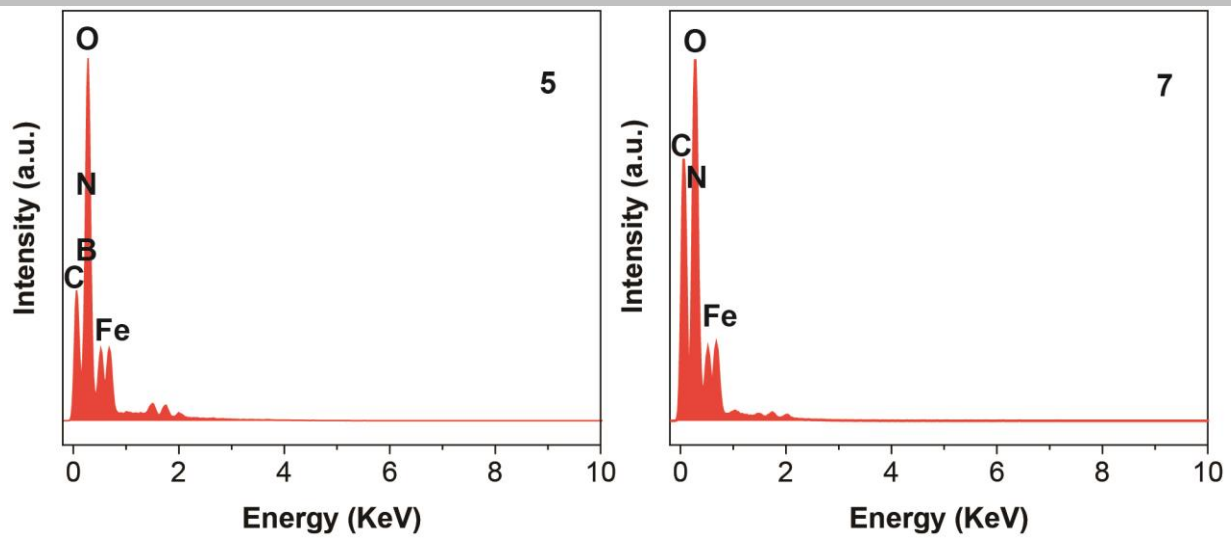


Figure S3. The SEM-EDX spectra of 5 and 7.

## 6. The cyclic voltammogram

Cyclic Voltammetry was performed under Ar atmosphere with a CHI600E potentiostat in a solution of anhydrous DMF with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, at a scan rate of 20, 50, 100, 200, 500 mV s<sup>-1</sup>. A glassy carbon was used as working electrode; a platinum wire was used as the auxiliary electrode, and an Ag/AgCl was used as reference electrode. Under these conditions,  $E_{1/2} = 0.56$  V for the FeCp<sub>2</sub><sup>+</sup>/FeCp<sub>2</sub> couple.

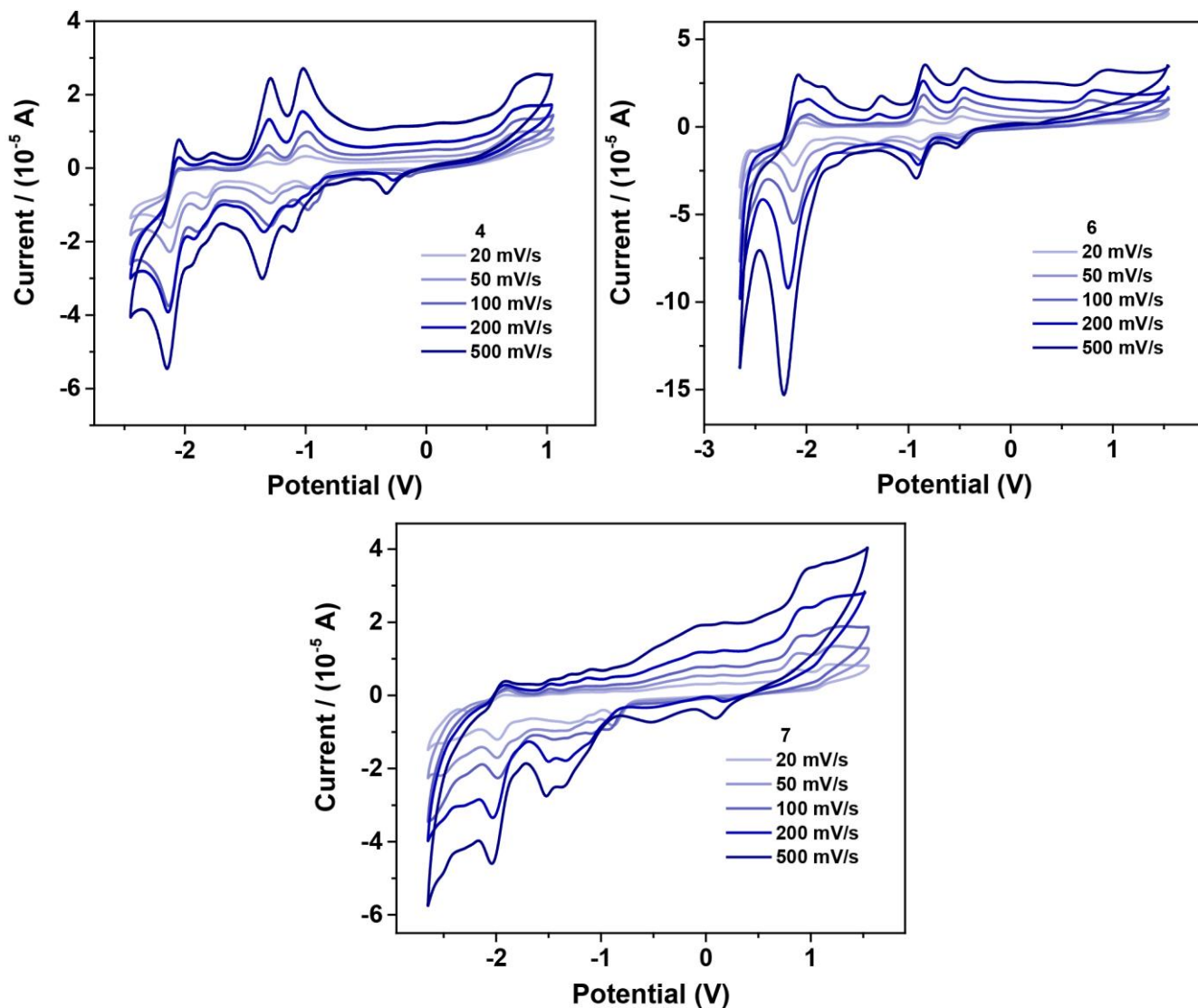


Figure S4 Cyclic voltammograms of 4, 6 and 7 recorded in DMF (10<sup>-3</sup> M)

**Table S4** Optical and Electronic Properties of **3 - 7**.

Compound	Electrochemical		LUMO (eV)		HOMO (eV)		Egap (eV)	
	$E_{red}$ (V)	$E_{ox}$ (V)	(Exp) <sup>[a]</sup>	(Calc) <sup>[b]</sup>	(Exp)	(Calc) <sup>[b]</sup>	(Exp) <sup>[c]</sup>	(Calc) <sup>[b]</sup>
<b>3</b>	-1.09, -1.43, -1.96, -2.08	-	-3.71	-2.91	-6.93	-7.78	3.22	4.87
<b>4</b>	-0.80, -1.15, -1.72, -2.03	0.52	-4.00	-2.93	-7.16	-6.90	3.16	3.97
<b>5</b>	-0.84, -1.14, -1.60, -1.95	0.62, 0.12	-3.96	-3.02	-5.67	-6.63	1.71	3.61
<b>6</b>	-0.35, -0.74, -1.72	0.50	-4.22	-3.86	-7.40	-7.15	3.18	3.29
<b>7</b>	-0.72, -1.01, -1.83	0.60, 0.11	-4.08	-3.74	-5.75	-6.65	1.67	2.91

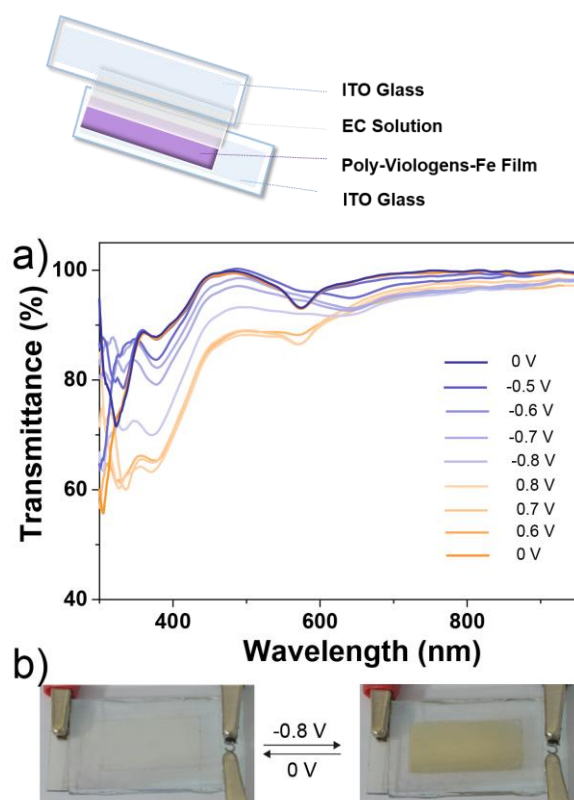
[a] Energy levels vs vacuum level were calculated from CV data and from the optically determined energy gap. [b] Theoretical calculations have been carried out by using the GAUSSIAN09 suite of programs. [c] Energy gap values were calculated from the absorption spectra

(1)  $E_{gap} = \frac{hc}{\lambda_{abs}} = \frac{1240}{\lambda_{abs}}$ ; (2)  $LUMO = -E_{red1} - 4.80$ ; (3)  $HOMO = LUMO + E_{gap}$ .

## 7. Electrochromism

In the solution-based ECD, indium-tin oxide (ITO)-coated glass ( $\sim 10 \Omega/\text{sq}$ ) was utilized as the electrodes and **5/7** was used as active component, 0.1M  $\text{LiClO}_4$  in water was acted as EC Solution.

Preparation of Fe-supramolecular polymers film. The Fe-supramolecular polymers film was prepared by the following step: firstly, preparing 3.0mg/mL solution of Fe-supramolecular polymers in NMP, and then filtrated with a microporous membrane; secondly, a ITO glass sized 2x3cm was placed on a hot plate at 70°C; thirdly about 200  $\mu\text{L}$  of Fe-supramolecular polymers in NMP solution was sprayed evenly onto the 2/3 area of ITO glass.



**Figure S5** a) Electrochemical spectra of **7** supramolecular polymer. b) Images of electrochromic device colour changes.

The optical stability for electrochromic switching of compound **3** and iron based supramolecular polymers **5** were tested between 0 and -3.0 V. The absorbance change is at 475 nm for **3** and at 630 nm for **5**. The coloring and bleach time were calculated with 90% total response time. The coloring efficiency ( $\eta$ ) was calculated with the following formula.

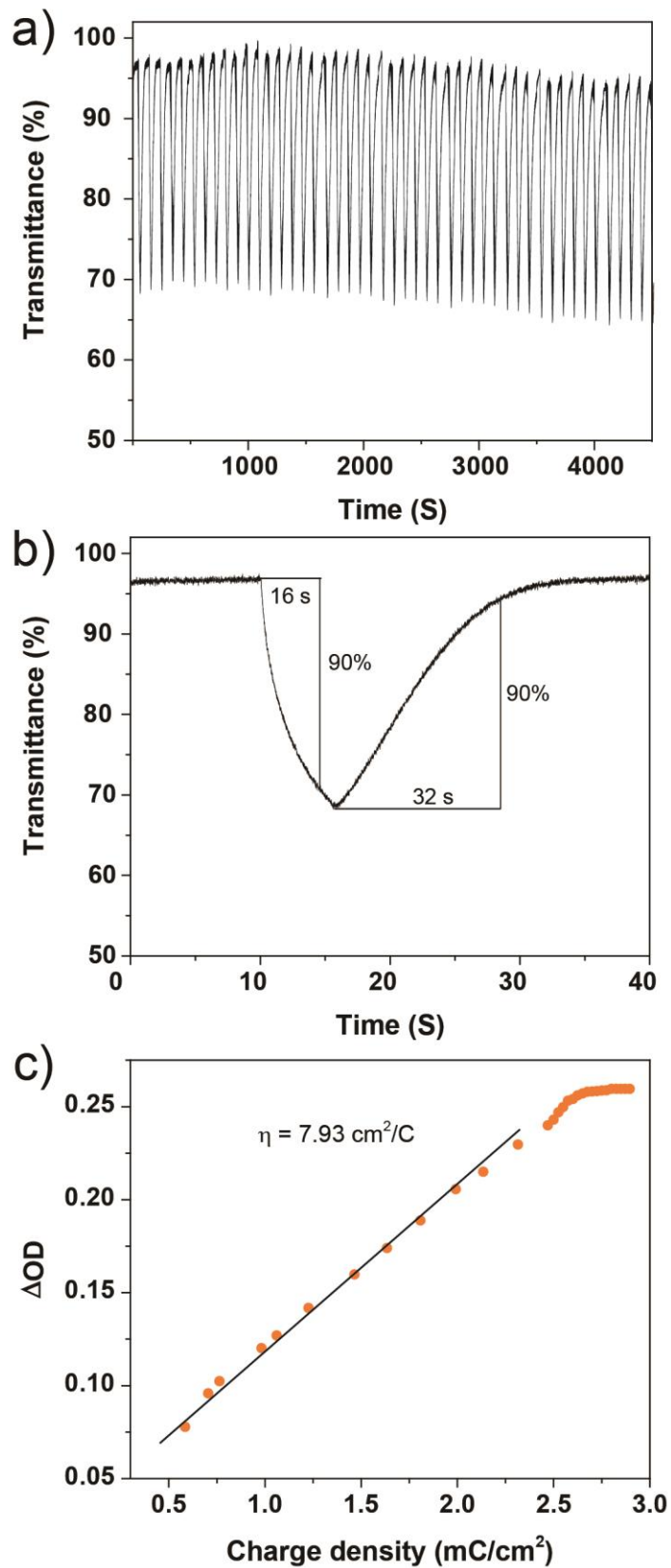
$$\eta = \Delta\text{OD}/Q \quad (1)$$

$$Q = \text{Areal}(t_1 - t_2) \quad (2)$$

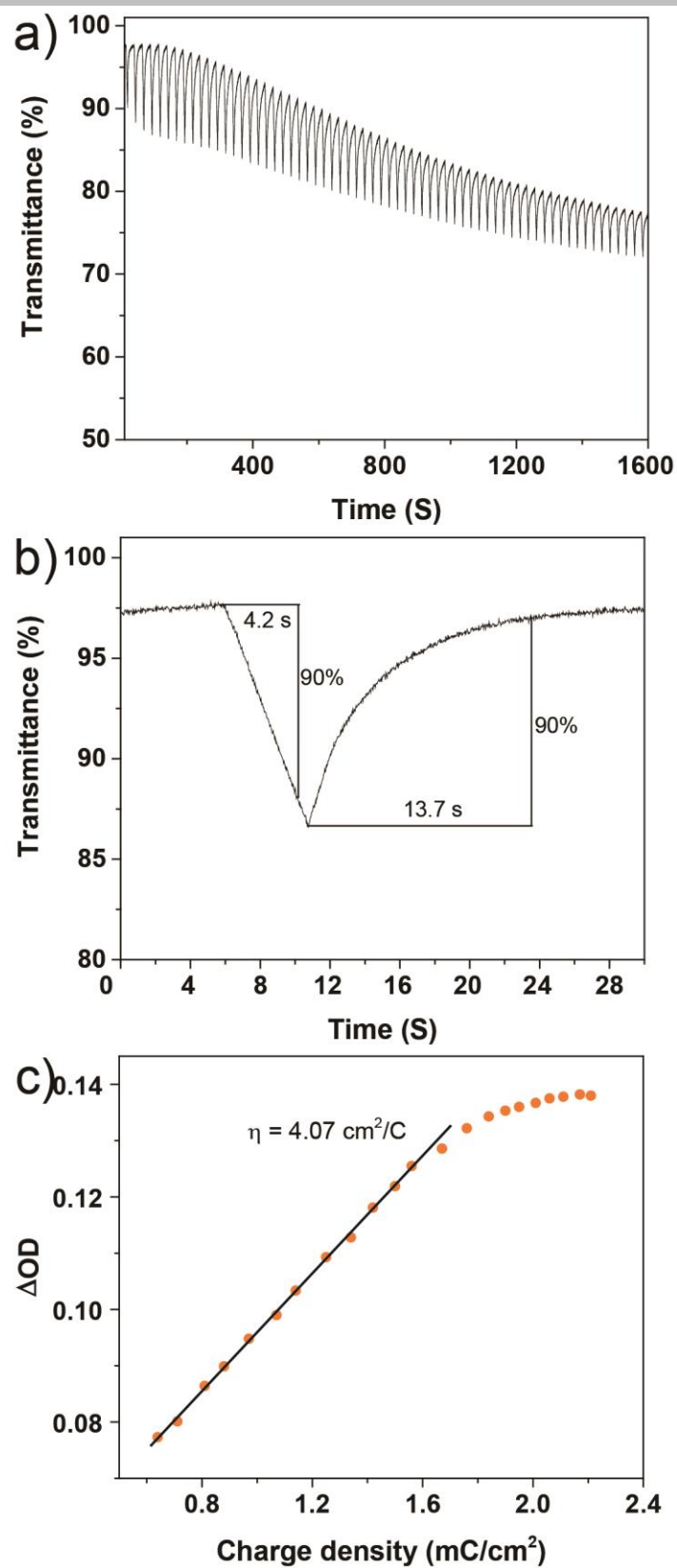
$$\Delta\text{OD} = \log(T_1/T_2) \quad (3)$$

For compound **3**, the coloring efficiency is  $7.93 \text{ cm}^2/\text{C}$ , the coloring time is 16 s and bleach time is 32 s.

For compound **5**, the coloring efficiency is  $4.07 \text{ cm}^2/\text{C}$ , the coloring time is 4.2 s and bleach time is 13.7 s.



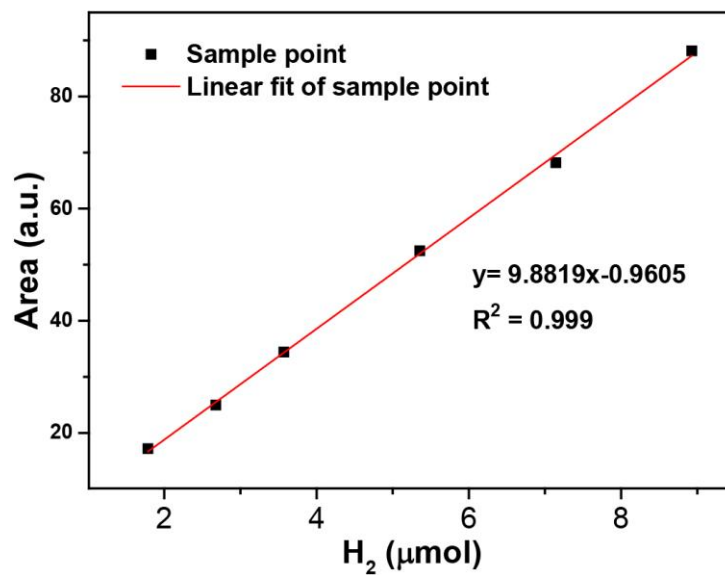
**Figure S6** a) optical stability test for electrochromic switching of **3**. b) Transmittance changes at 475 nm of **3** ECD. c) The coloring efficiency of **3** ECD.



**Figure S7** a) optical stability test for electrochromic switching of **5**. b) Transmittance changes at 630 nm of **5** ECD. c) The coloring efficiency of **5** ECD.

## 8. H<sub>2</sub> normalized curve

The system in which H<sub>2</sub> was 1.0 percent (volume fraction) and protected by Argon was chosen as the "standard H<sub>2</sub>". 40 μL, 60 μL, 80 μL, 120 μL, 160 μL, 200 μL gas from the "standard H<sub>2</sub>" was injected to GC respectively, every volume for three times. The curve figure was the H<sub>2</sub> peak area verse the number of moles of hydrogen and the equation was fitted by origin.



**Figure S8** H<sub>2</sub> peak area verse the number of moles of hydrogen and polynomial fit of sample point to be H<sub>2</sub> normalized curve.

## 9. Hydrogen generation under xenon lamp

The mixed aqueous solution containing **5/7** (2 mg), EDTA (0.5 nmol) and PVP-Pt (5 mg) was sealed in the 20 mL Pyrex bottle with a rubber stopper. The solution was bubbled with Argon for 30 min, after that it was irradiated under Xenon lamp ( $> 400$  nm) with light power of 100 mW. Then 200  $\mu$ L upper gas of the reactor was injected to gas chromatography two hour to measure hydrogen generation. The production of the hydrogen was calculated according to the  $H_2$  normalized curve (Fig. S8).

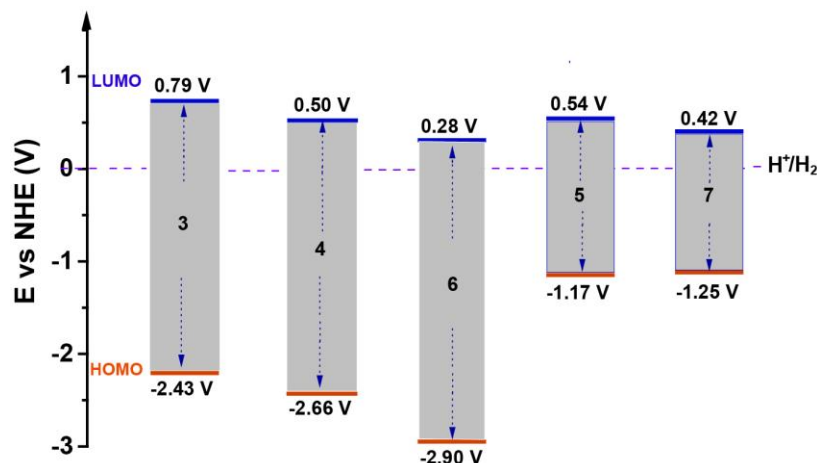


Figure S9 Experimental energy levels of the LUMO and HOMO orbitals for **3 - 7** vs NHE

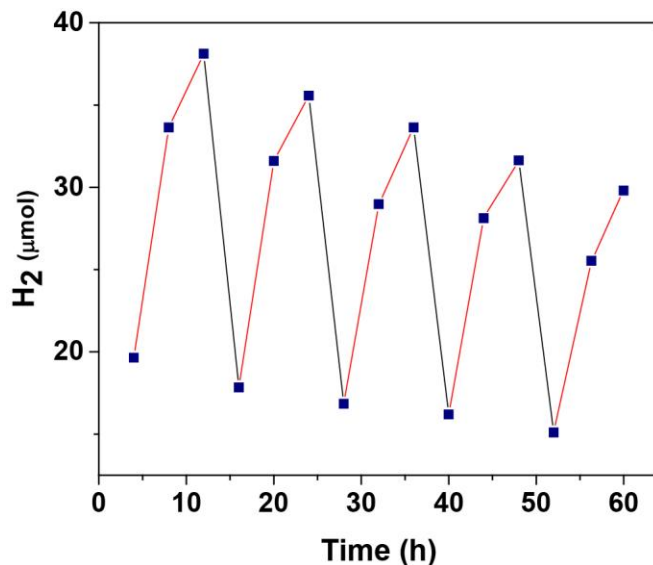


Figure S10 Hydrogen generation of **5** system upon five cycles (every twelve hours is a cycle)

### Apparent quantum yield (AQY) calculation:

For the max of the absorption of **5** is 574 nm, in the equation (1),  $\lambda = 574$  nm. E is measured 100 mW. The number of incident photons ( $N_0$ ) is calculated to be  $2.88 \times 10^{17} \text{ s}^{-1}$  by equation (1). The  $H_2$  molecules generated in 24 h under Xenon light was 41.91  $\mu$ mol. The photons number of collected to be  $H_2$  is  $2.92 \times 10^{14} \text{ s}^{-1}$  as calculated by equation (2). The AQY is  $2.03 \times 10^{-3}$  calculated by equation(3):

$$N_0 = \lambda E/hc = 574 \times 10^{-9} \times 100 \times 10^{-3} / (6.63 \times 10^{-34} \times 3 \times 10^8) \text{ s}^{-1} = 2.88 \times 10^{17} \text{ s}^{-1} \quad (1)$$

$$N = nNA/t = 41.91 \times 10^{-6} \times 6.02 \times 10^{23} / (24 \times 3600) \text{ s}^{-1} = 2.92 \times 10^{14} \text{ s}^{-1} \quad (2)$$

$$\text{AQY}(\mathbf{5}) = 2N/N_0 = 2.03 \times 10^{-3} \quad (3)$$

For the max of the absorption of **7** is 576 nm,  $N_0 = 2.89 \times 10^{17} \text{ s}^{-1}$ ,  $N = 1.53 \times 10^{14} \text{ s}^{-1}$ ,  $\text{AQY}(\mathbf{5}') = 1.05 \times 10^{-3}$



**Table S5** Hydrogen generation activities of some organic photocatalytic system.

Classify	Catalysts	Hydrogen generation rate	Apparent Quantum yield	Conditions	Reference
Viologen-containing photocatalytic HER system	MV(NO <sub>3</sub> ) <sub>2</sub> {[Ru(bpy) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> •3H <sub>2</sub> O, Co(dmgH) <sub>2</sub> (pyridine)Cl] <sup>[5]</sup>	0.016 mmol•h <sup>-1</sup> •g <sup>-1</sup>	---	aqueous acetate buffer solution (0.03 M CH <sub>3</sub> COOH and 0.07 M CH <sub>3</sub> COONa)	<i>Chem. Commun.</i> , 2014, <b>50</b> , 9872–9875
	PBDT-BPY (10–20% CoCl <sub>2</sub> ) <sup>[6]</sup>	0.14 mmol•h <sup>-1</sup> •g <sup>-1</sup>	0.025%	30 vol% diethylamine/water	<i>Chem. Mater.</i> , 2016, <b>28</b> , 5394–5399
	PPDI-bpy (~60% CoCl <sub>2</sub> ) <sup>[6]</sup>	0.36 mmol•h <sup>-1</sup> •g <sup>-1</sup>	0.017%	30 vol% diethylamine/water	<i>Chem. Mater.</i> , 2016, <b>28</b> , 5394–5399
	[PtCl <sub>2</sub> (dpbpy MV <sub>4</sub> )]Cl <sub>8</sub> •16H <sub>2</sub> O <sup>[7]</sup>	0.33 mmol•h <sup>-1</sup> •g <sup>-1</sup>	---	aqueous acetate buffer solution (0.03 M CH <sub>3</sub> COOH and 0.07 M CH <sub>3</sub> COONa)	<i>Chem. Commun.</i> , 2016, <b>52</b> , 1385–1388
	MV <sup>2+</sup> (PT) <sup>[8]</sup>	0.074 mmol•h <sup>-1</sup> •g <sup>-1</sup>	0.064%	Pure aqueous λ > 420 nm	<i>ACS Appl. Mater. Interfaces</i> , 2017, <b>9</b> , 10355–10359
	Se-PhV <sup>2+</sup> <sup>[9]</sup>	0.71 mmol•h <sup>-1</sup> •g <sup>-1</sup>	0.11%	aqueous acetate buffer solution λ > 400 nm	<i>J. Mater. Chem. A</i> , 2020, <b>8</b> , 12278–12284.
Viologen based-metallo-supramolecular polymer	<b>5</b>	0.87 mmol•h <sup>-1</sup> •g <sup>-1</sup>	0.23%	aqueous acetate buffer solution λ > 400 nm	This work
	<b>7</b>	0.46 mmol•h <sup>-1</sup> •g <sup>-1</sup>	0.15%	aqueous acetate buffer solution λ > 400 nm	This work

## 10. Computed UV-vis spectra.

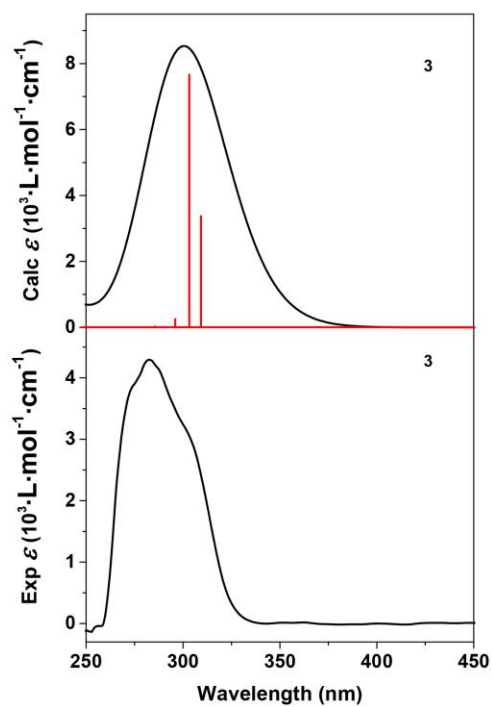


Figure S11 Computed at the PCM(DMF)// TD-PBE0/6-31G\* //PBE0/6-31G\* level of theory, and experimental UV-vis spectra of 3.

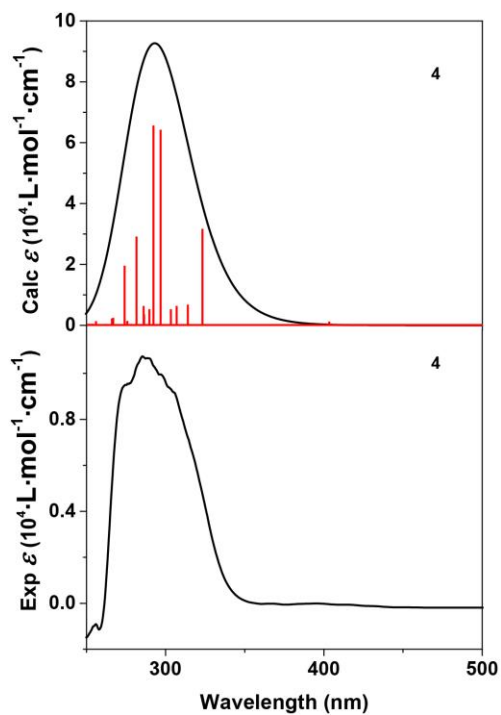
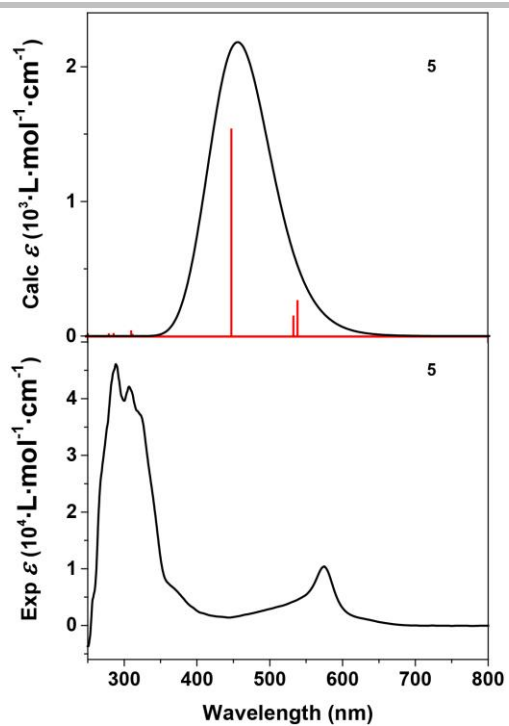
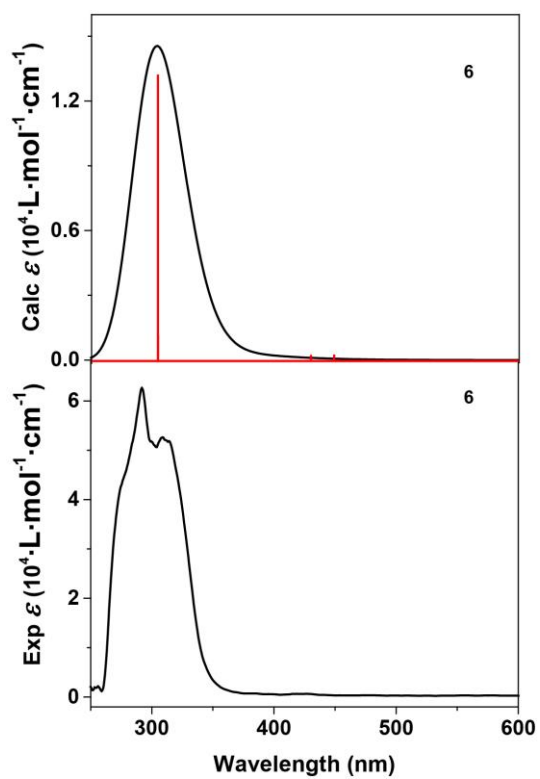


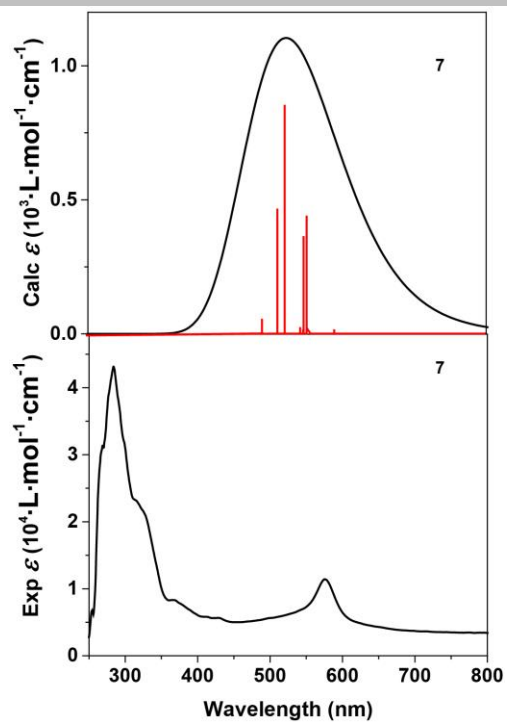
Figure S12. Computed at the PCM(DMF)// TD-PBE0/6-31G\* //PBE0/6-31G\* level of theory, and experimental UV-vis spectra of 4.



**Figure S13** Computed at the PCM(DMF)// TD-PBE0/6-31G\* //PBE0/6-31G\* level of theory, and experimental UV-vis spectra of **5**.



**Figure S14** Computed at the PCM(DMF)// TD-PBE0/6-31G\* //PBE0/6-31G\* level of theory, and experimental UV-vis spectra of **6**.



**Figure S15** Computed at the PCM(DMF)// TD-PBE0/6-31G\* //PBE0/6-31G\* level of theory, and experimental UV-vis spectra of 7.

## 11. DFT Calculations (PBE0/6-31G\*)

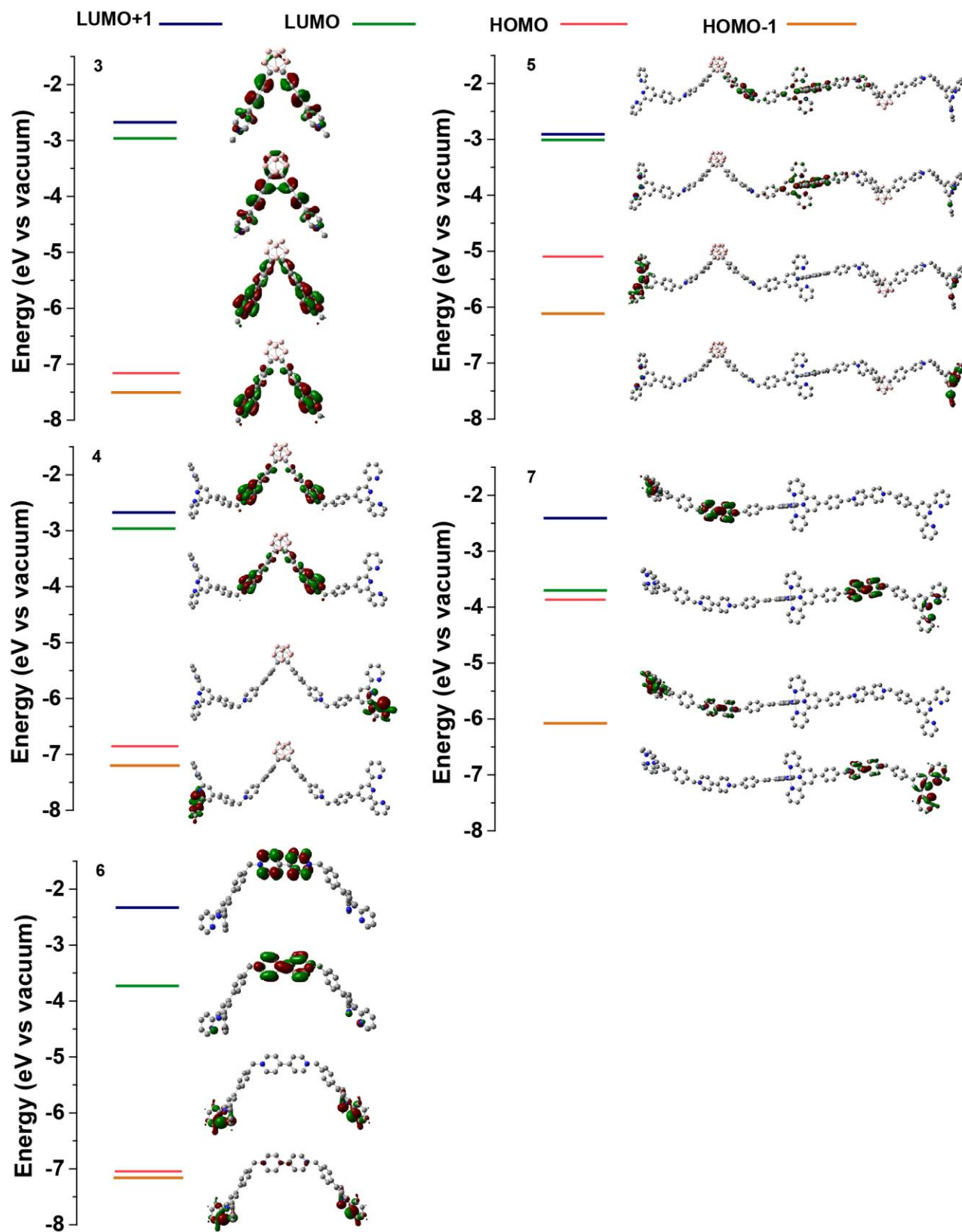
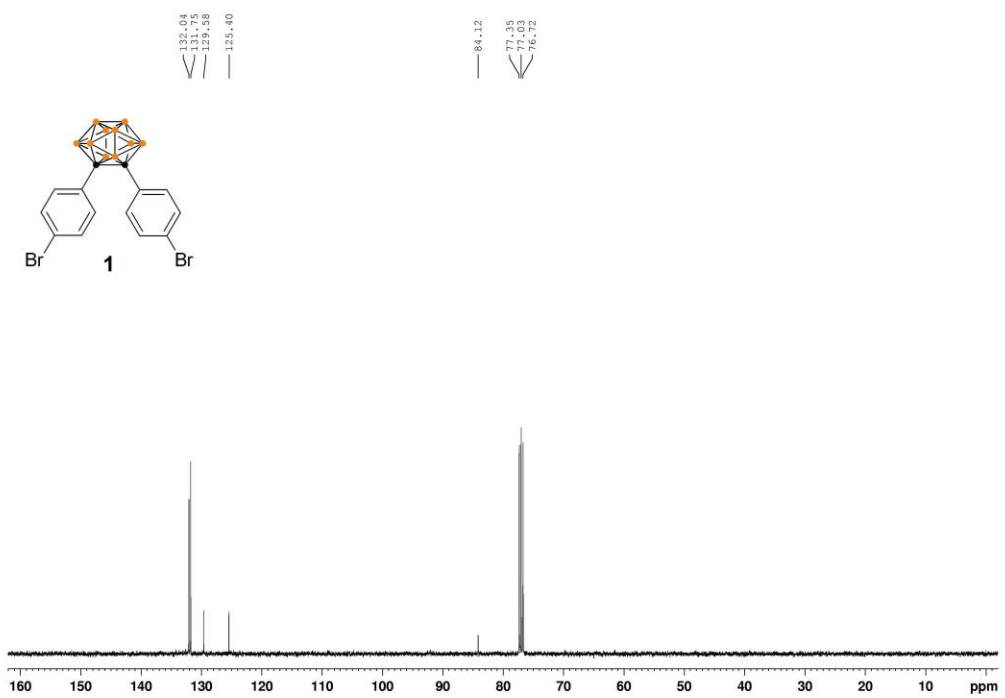
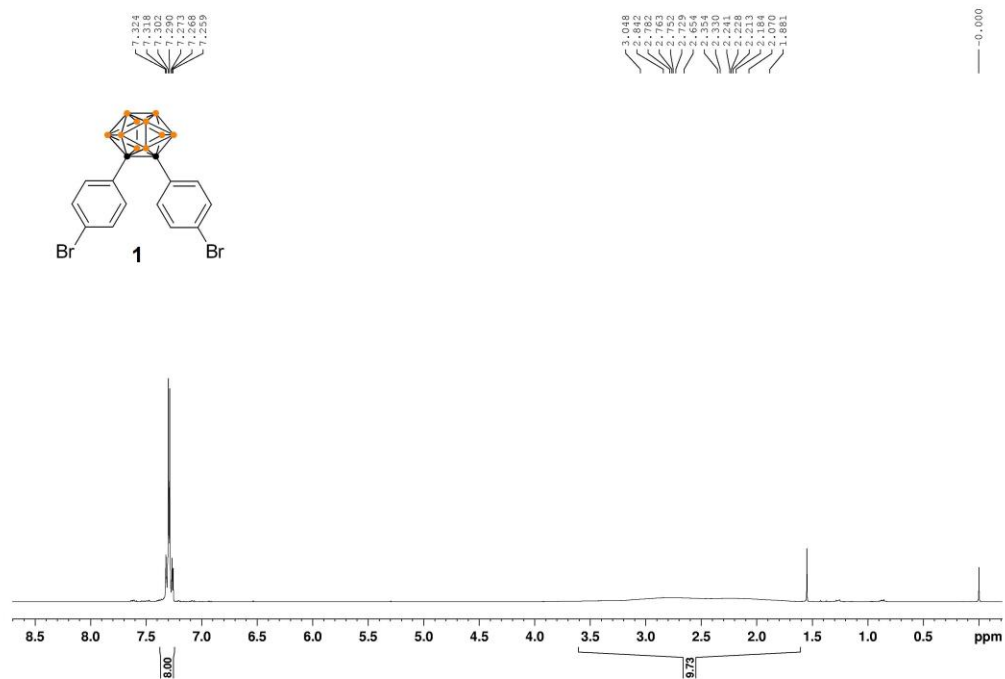
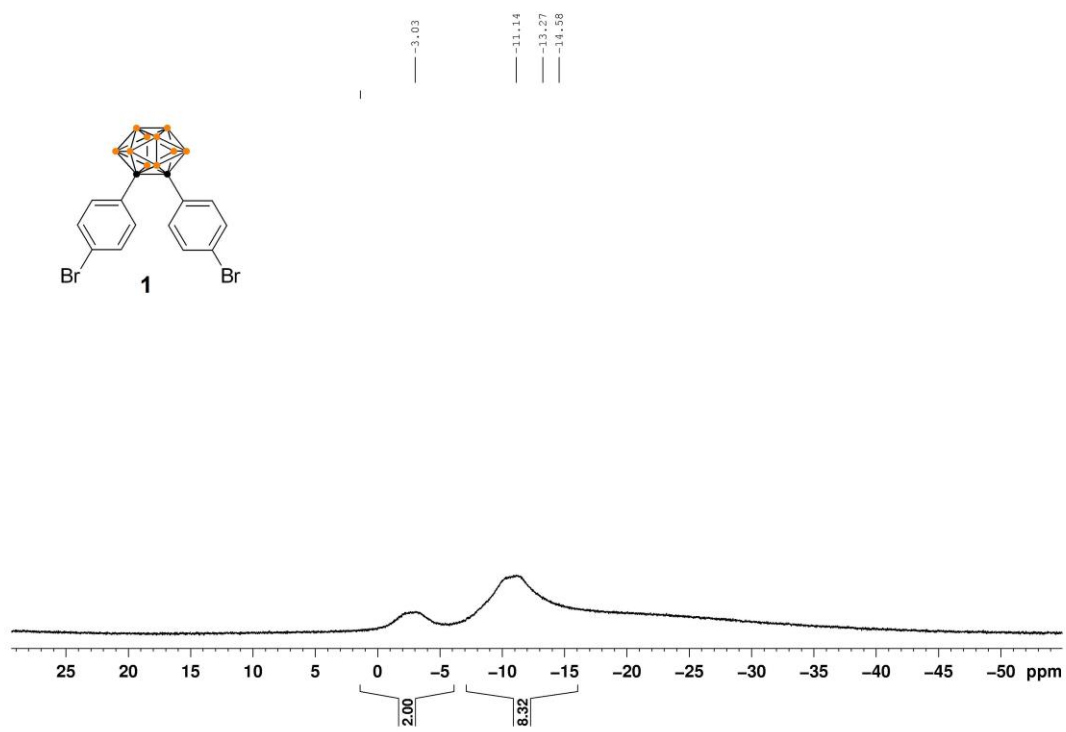


Figure S16 HOMO-1, HOMO, LUMO, and LUMO+1 energy levels of **3** - **7** (isosurface values  $\pm 0.03$ )

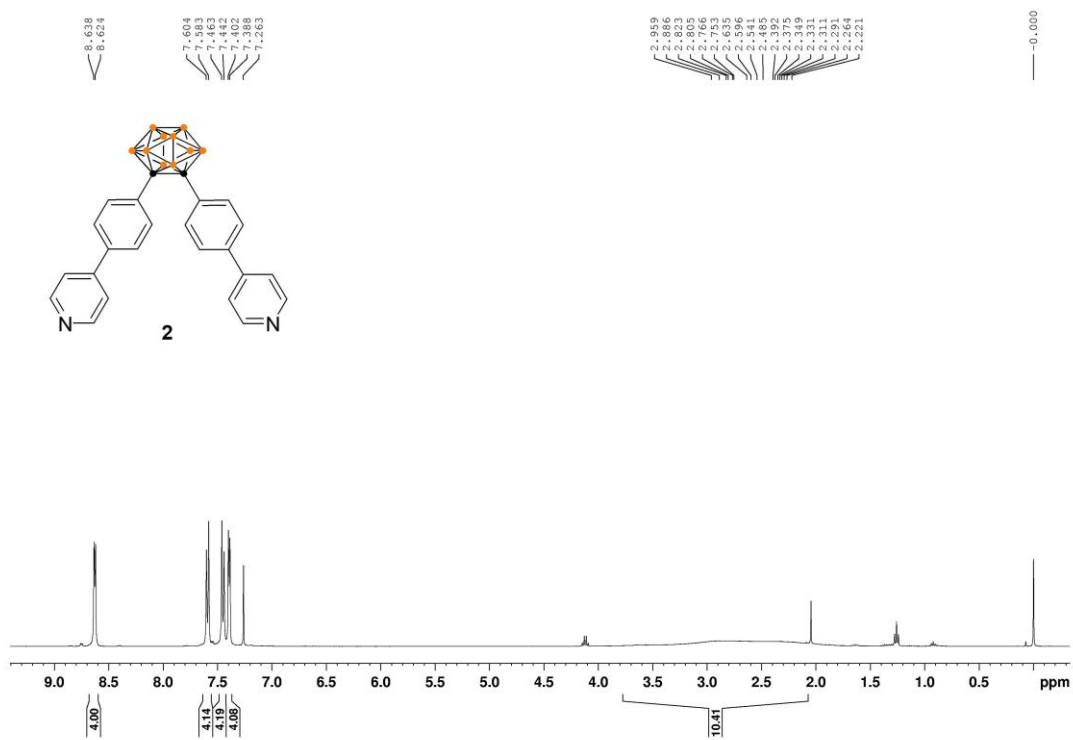
## 12. $^1\text{H}$ , $^{13}\text{C}$ , $^{11}\text{B}$ $^{19}\text{F}$ NMR spectra

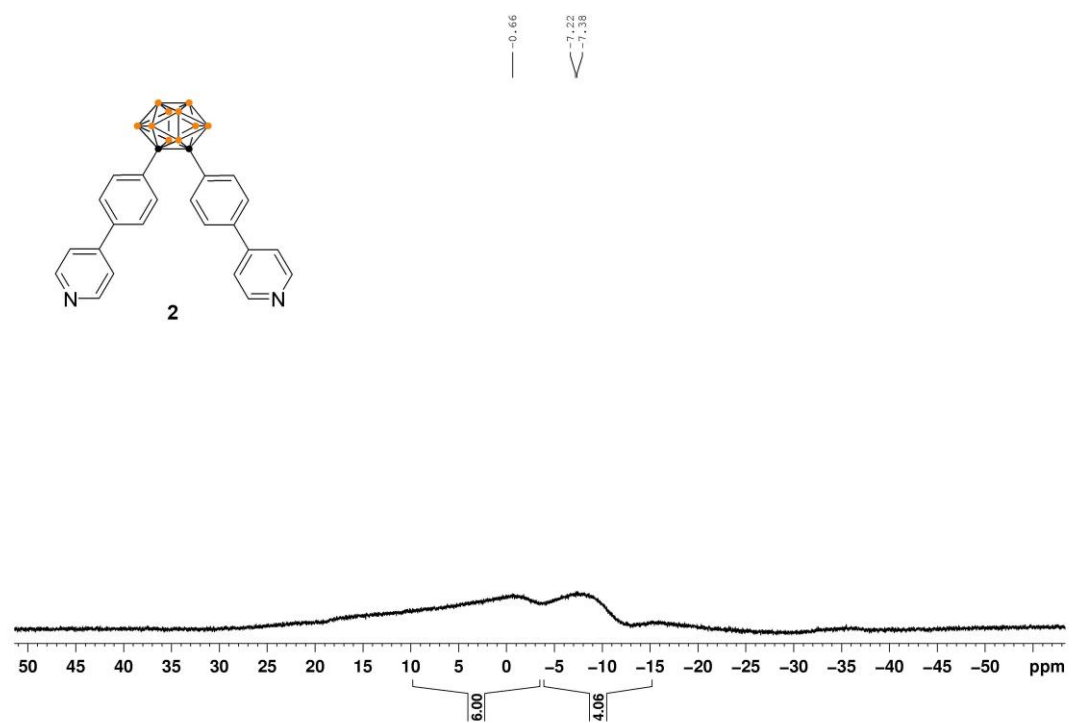
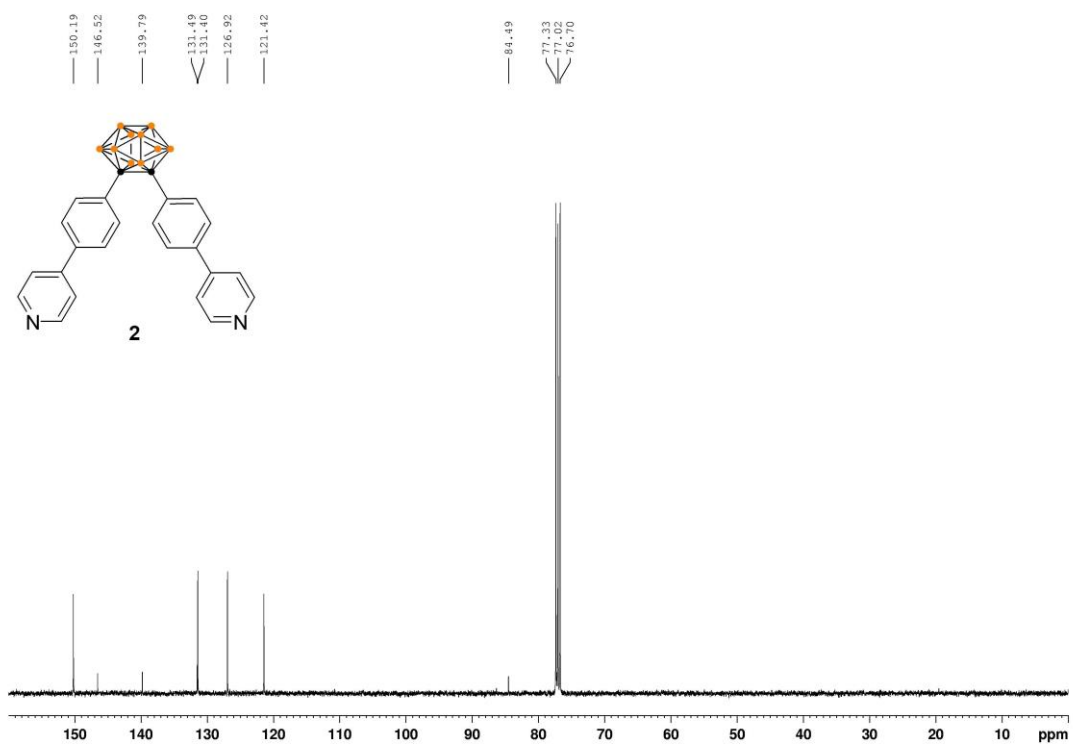
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz) and  $^{11}\text{B}$   $\{^1\text{H}\}$  spectra of **1**





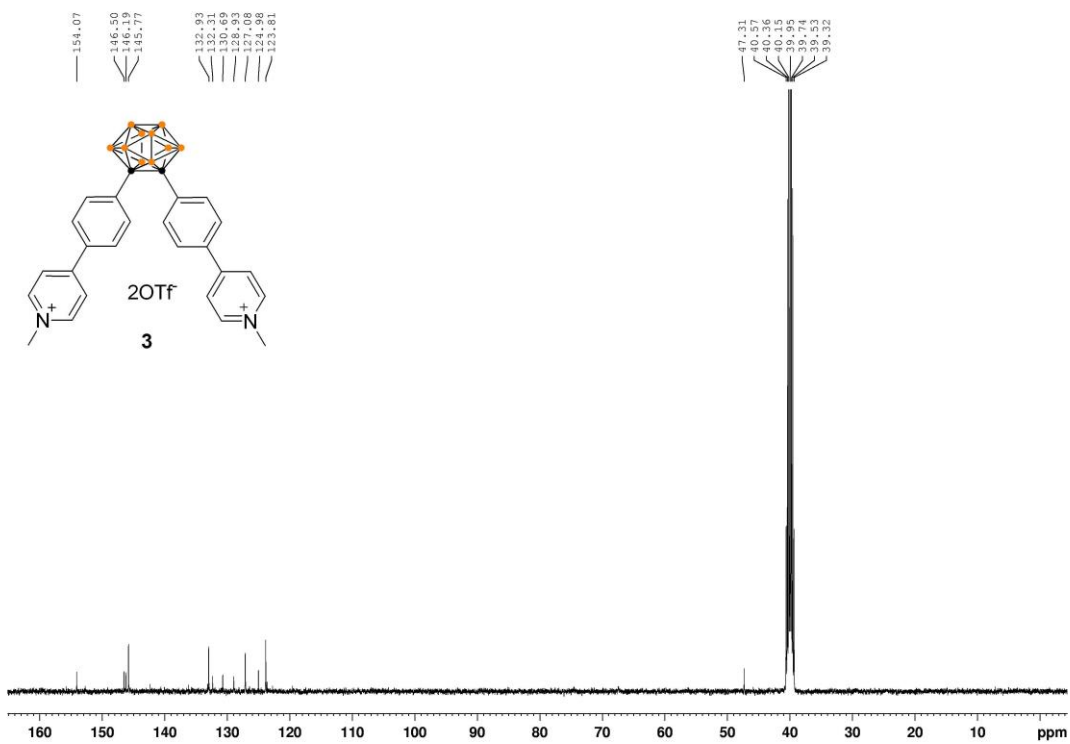
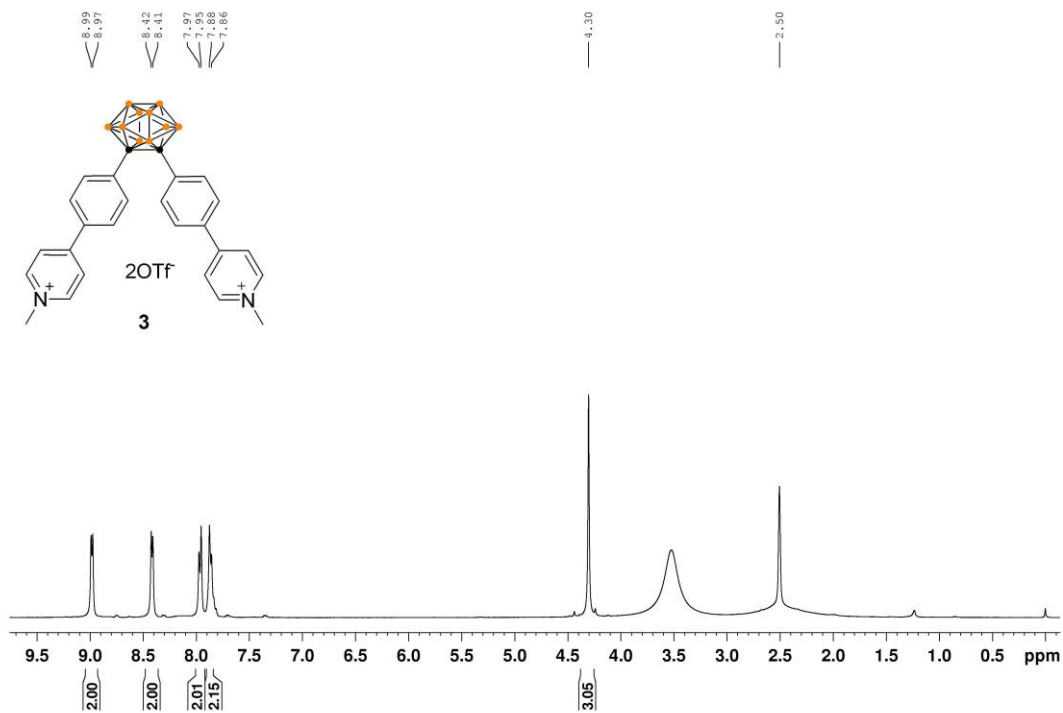
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) and <sup>11</sup>B {<sup>1</sup>H} spectra of **2**

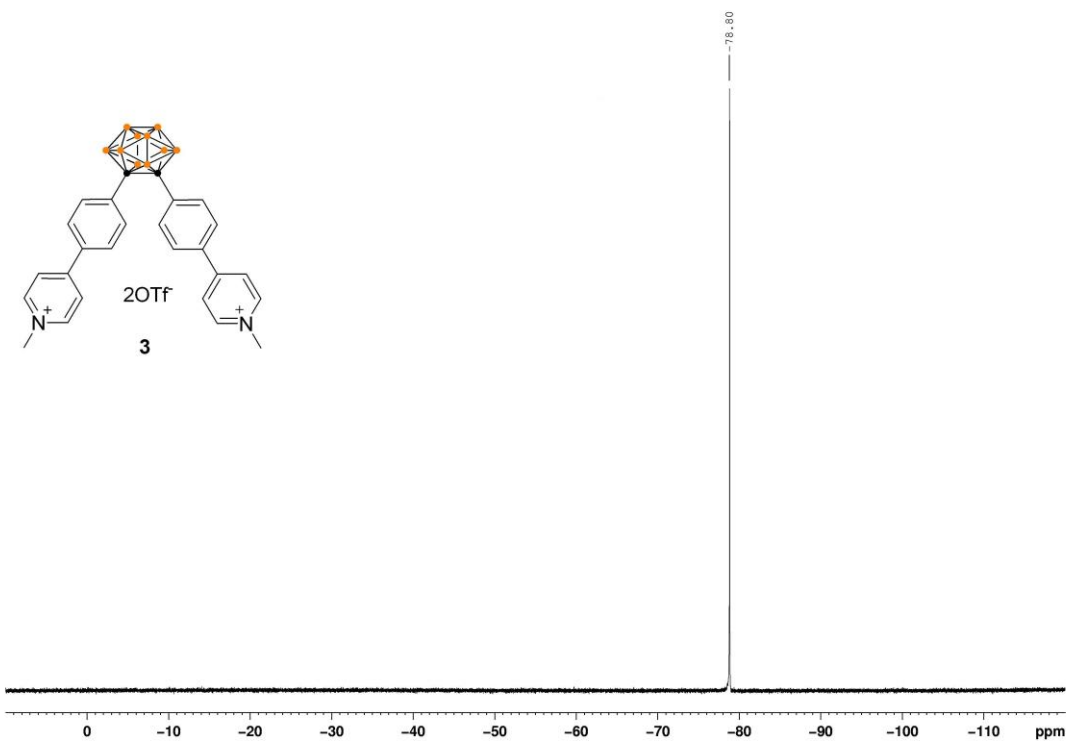
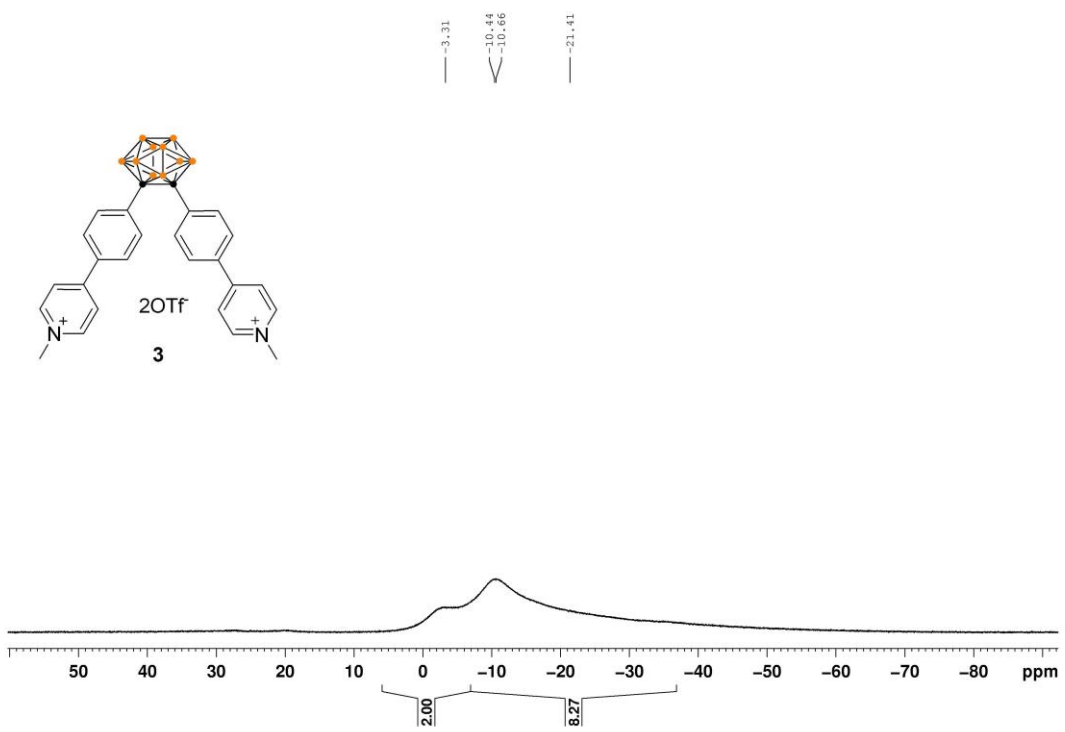




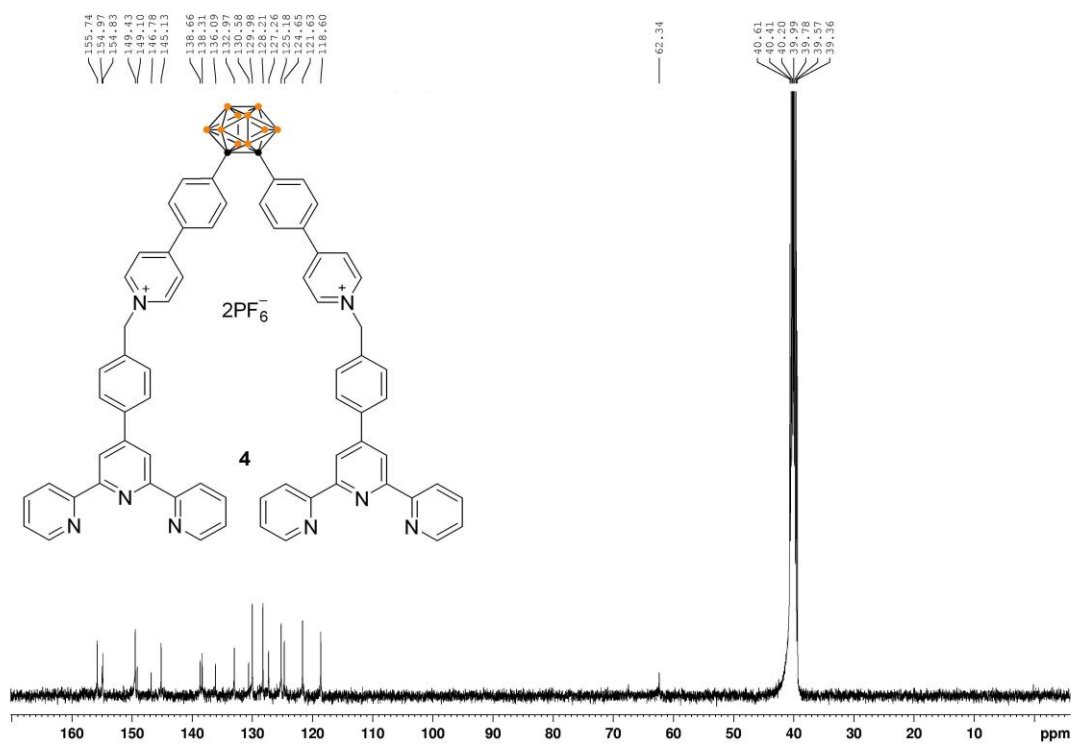
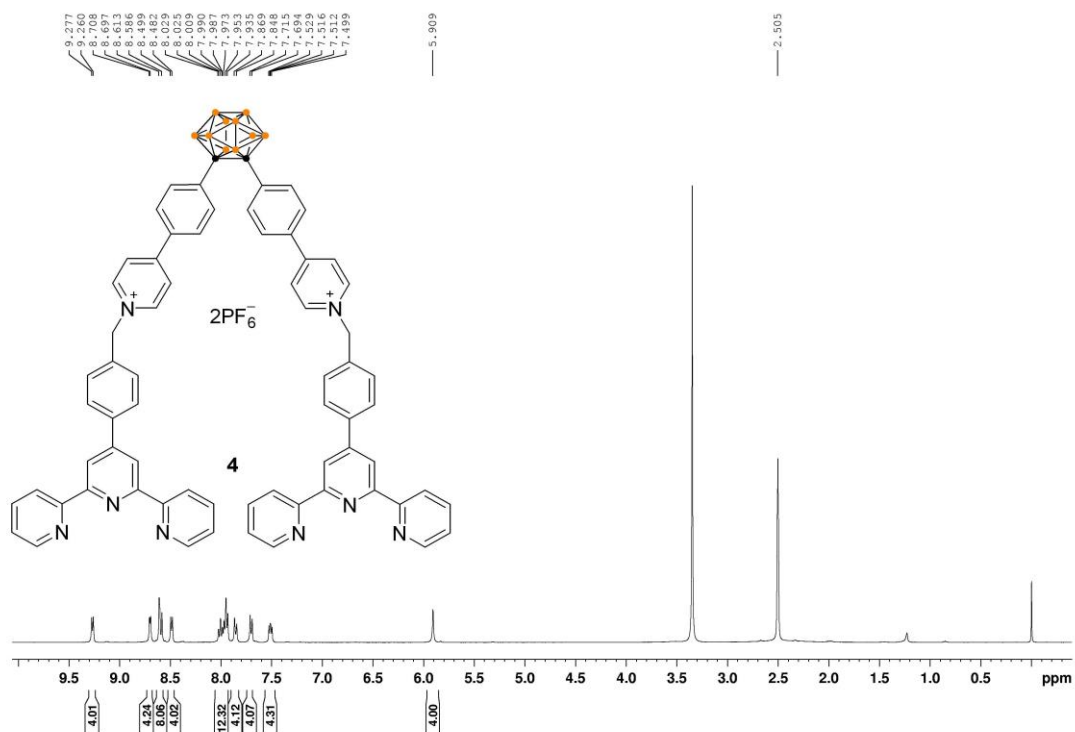


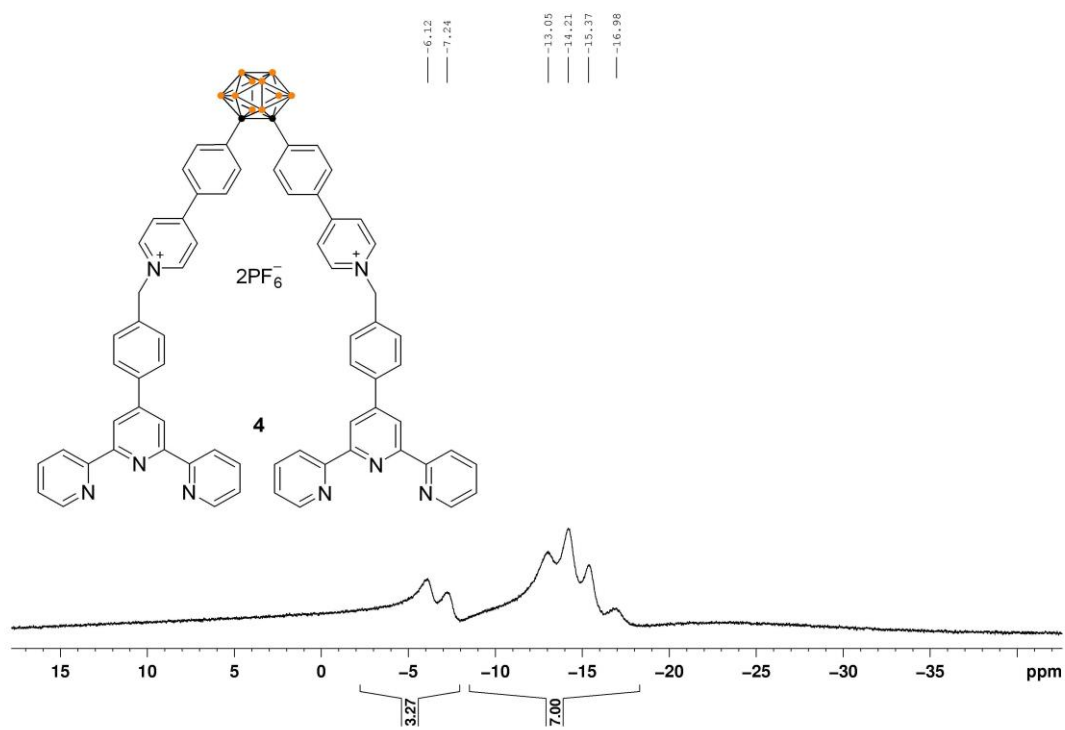
$^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz),  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz),  $^{11}\text{B}$  { $^1\text{H}$ } and  $^{19}\text{F}$  NMR (DMSO- $d_6$ , 376 MHz) spectra of **3**.



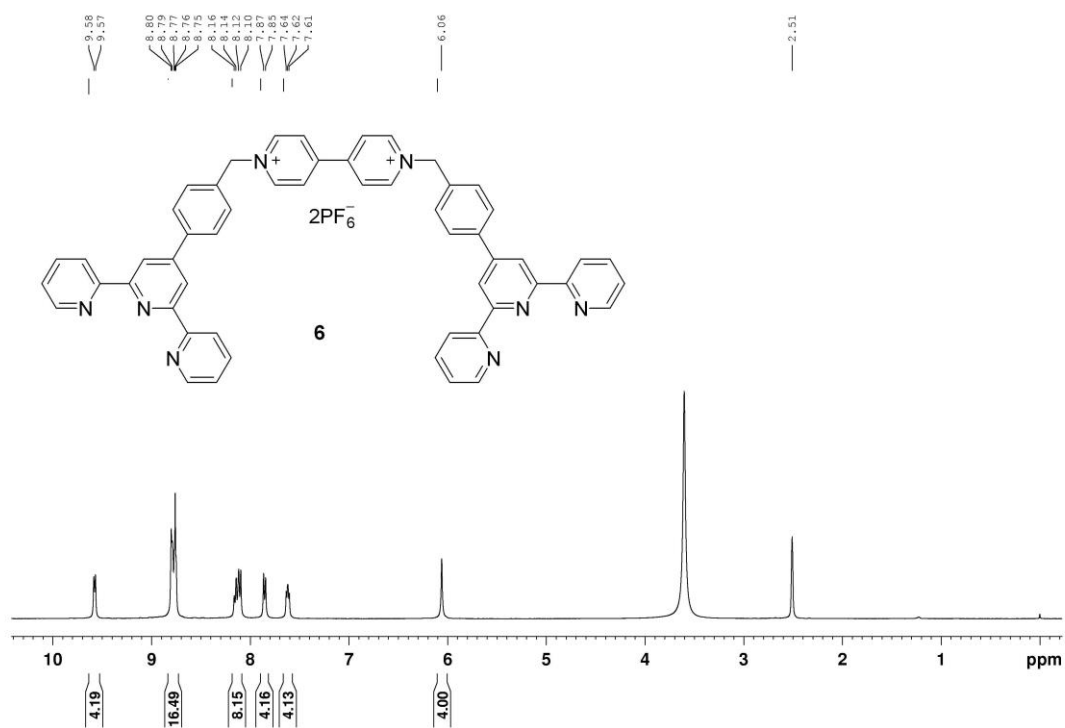


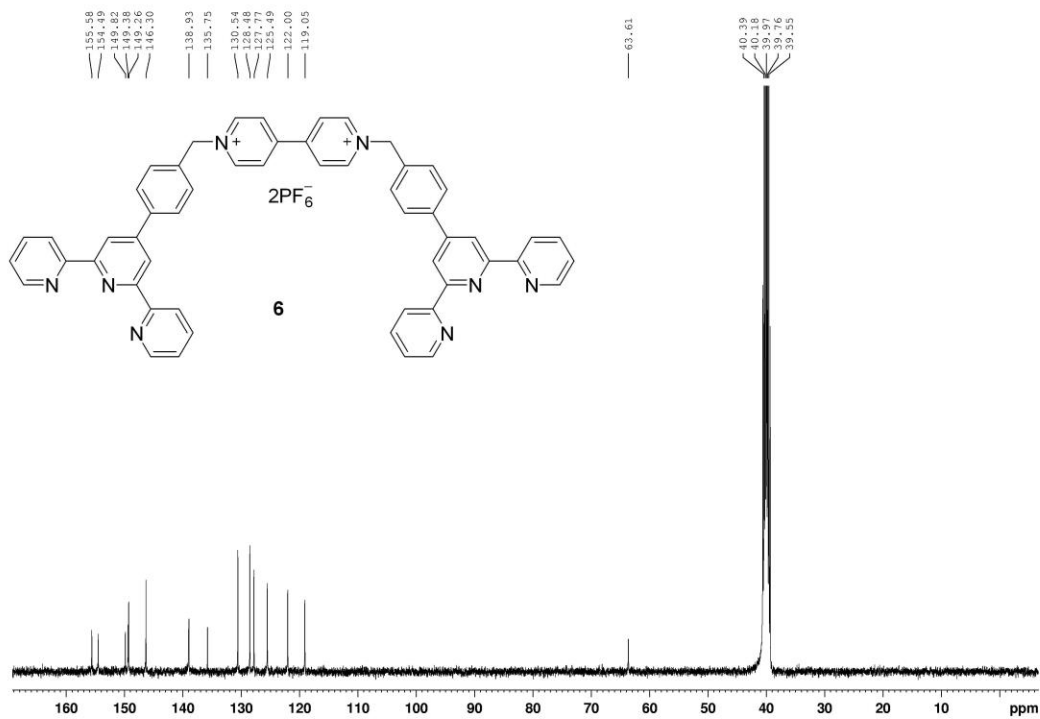
$^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz),  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz), and  $^{11}\text{B}$   $\{^1\text{H}\}$  spectra of **4**



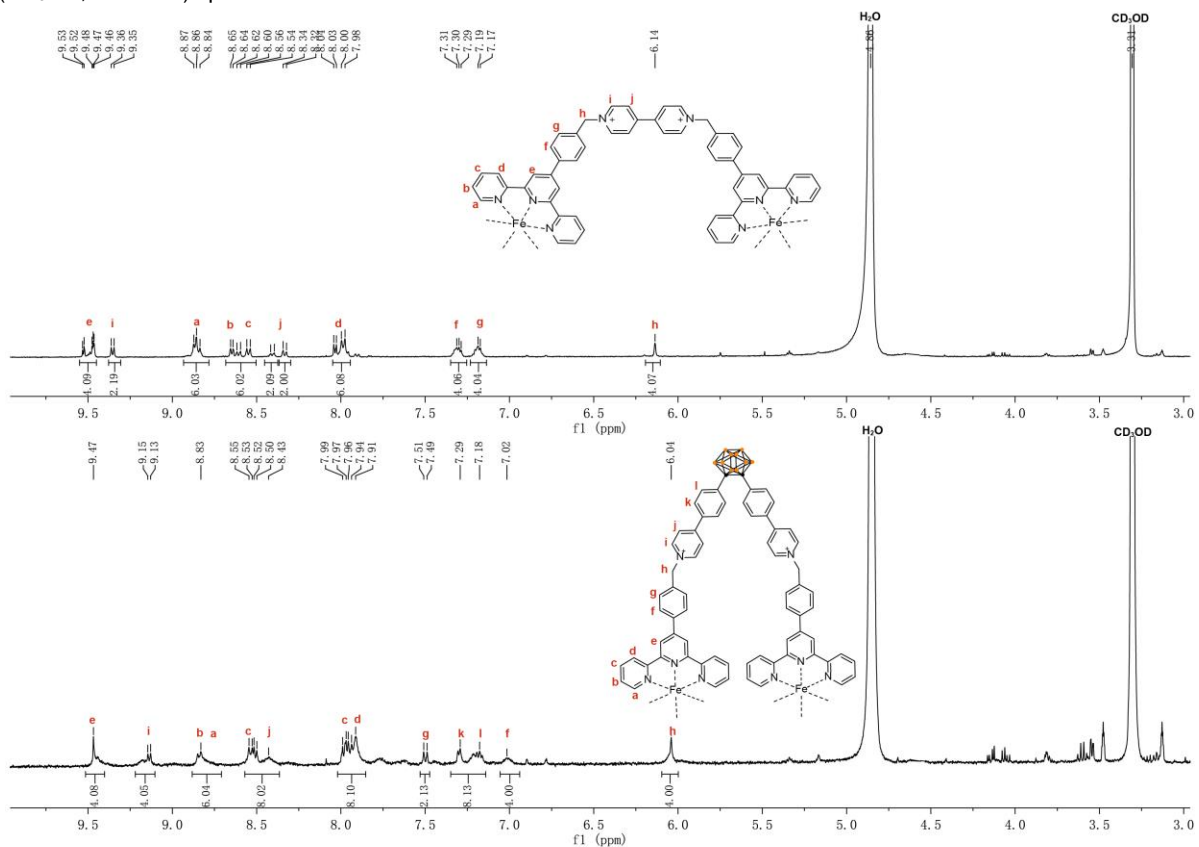


$^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz),  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz) and  $^{11}\text{B}$   $\{^1\text{H}\}$  spectra of **6**



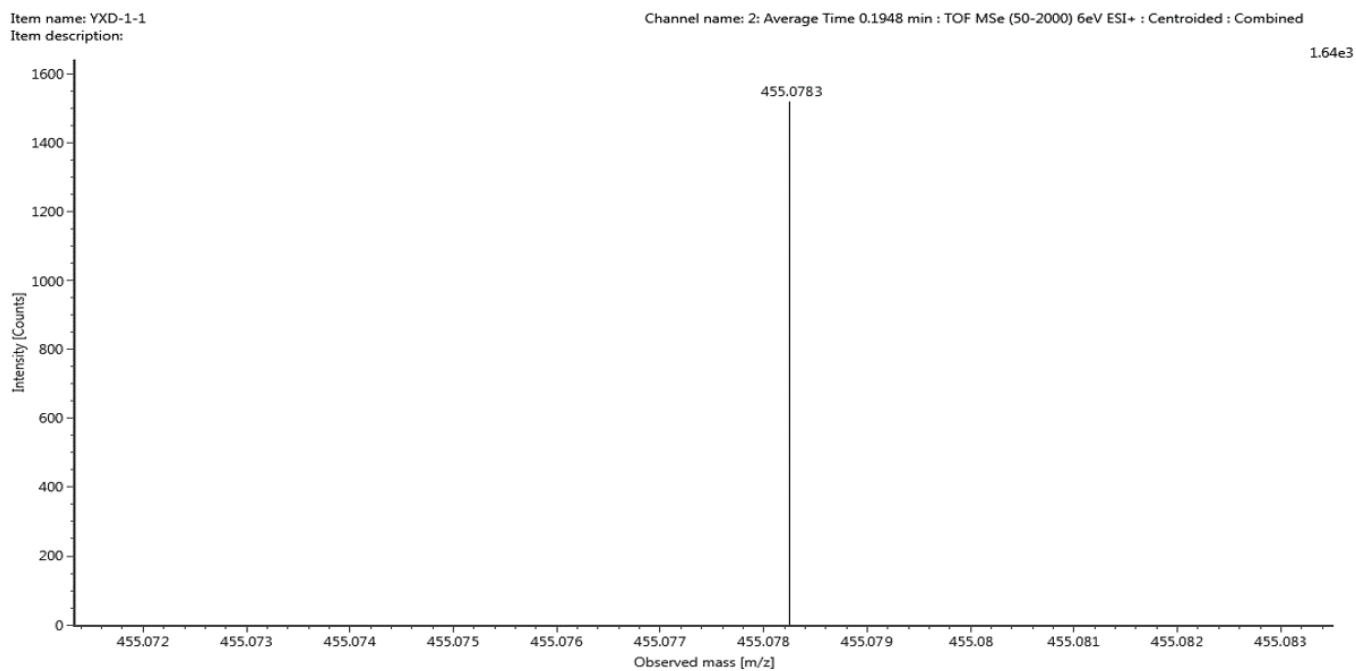


$^1H$  NMR ( $CD_3OD$ , 400 MHz) spectra of **5** and **7**

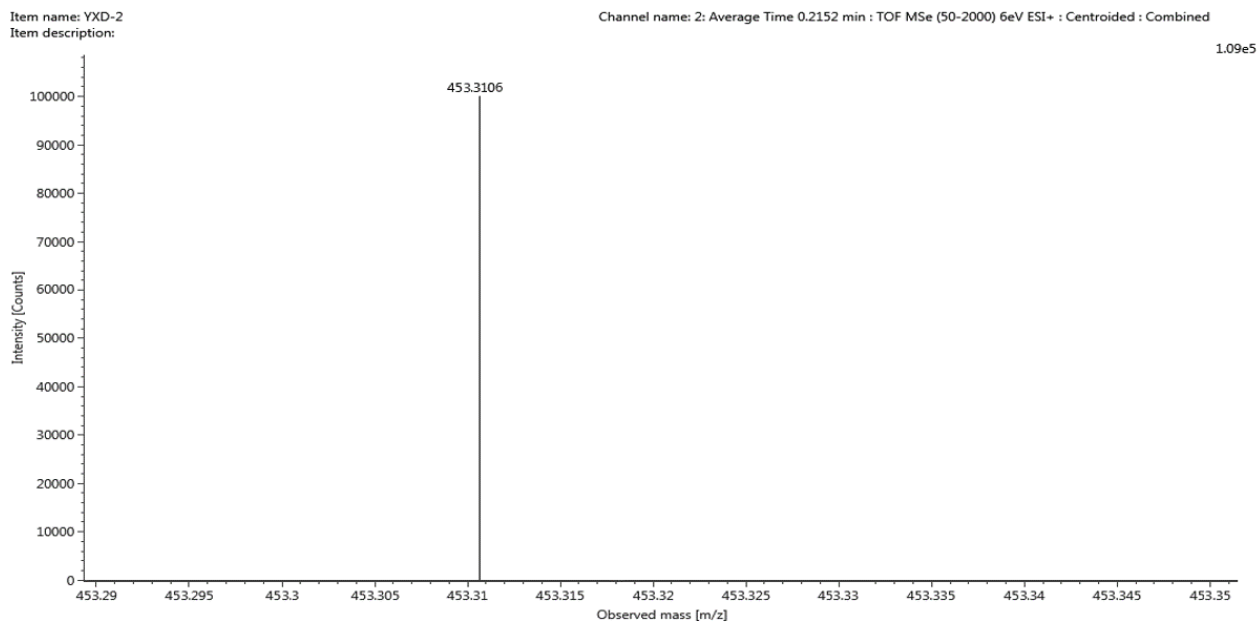


### 13. The HRMS spectra

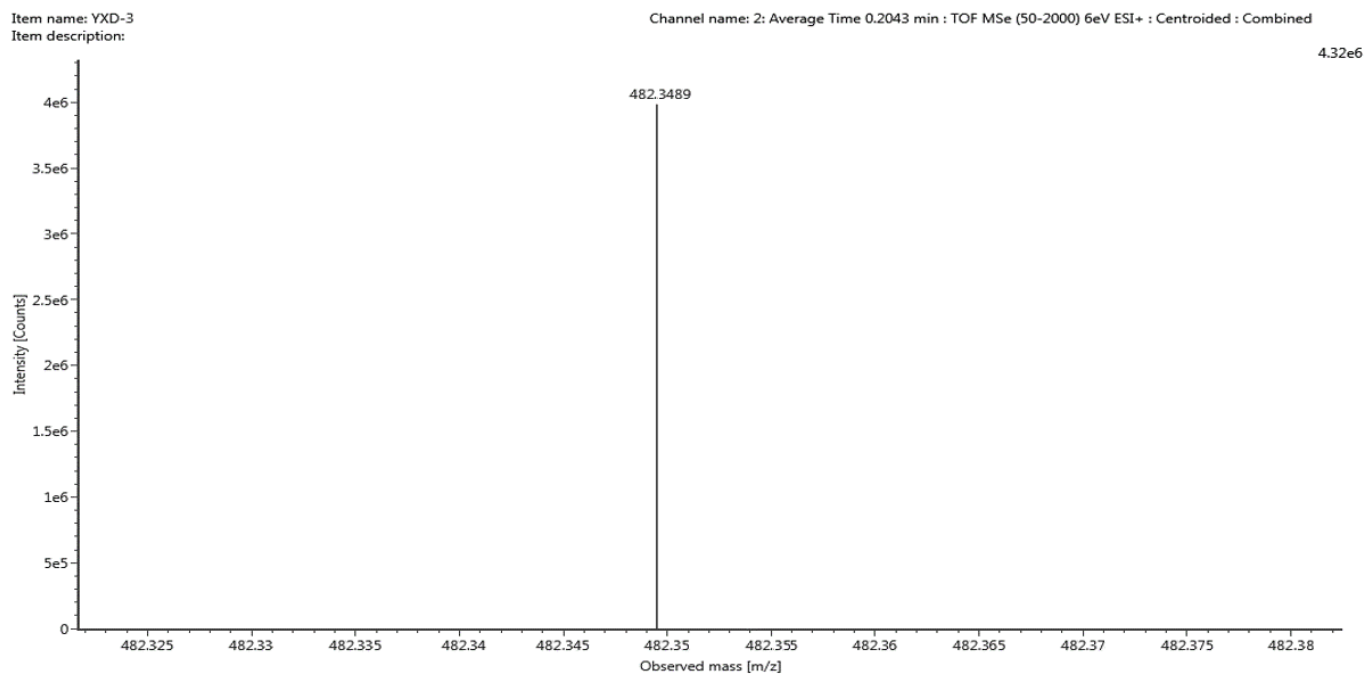
#### The HRMS spectra of 1



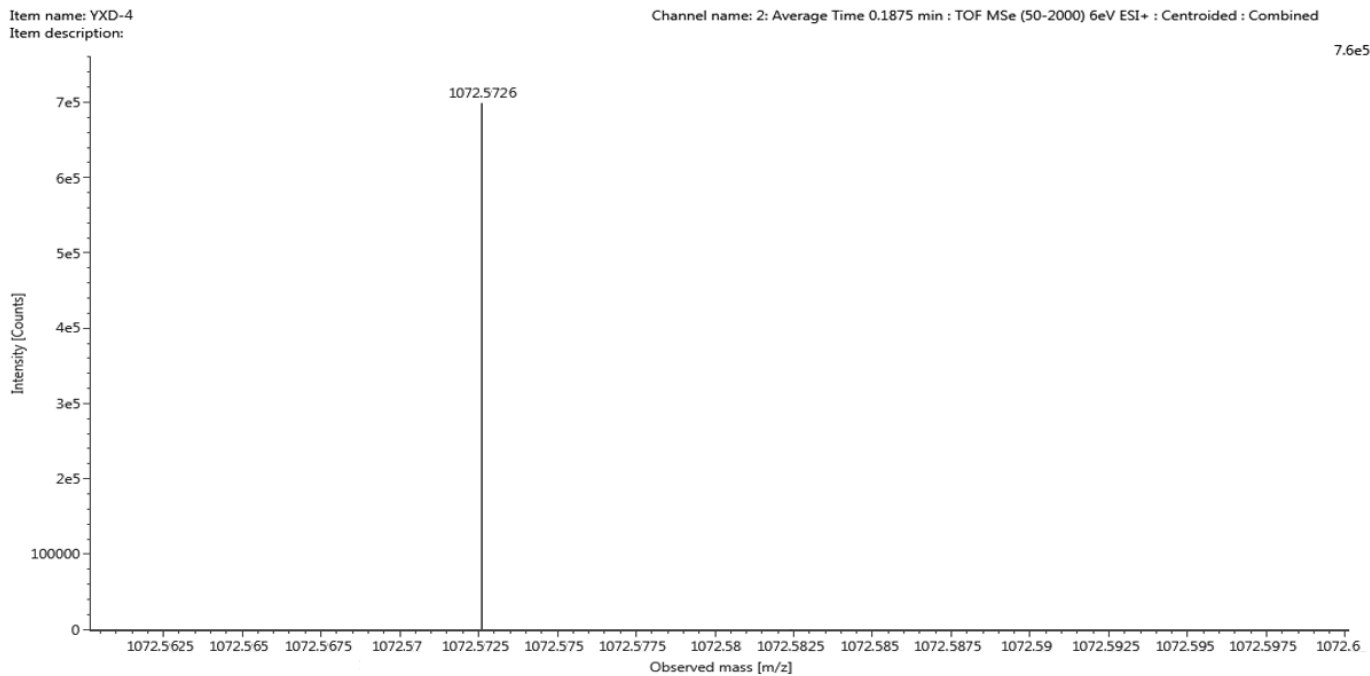
#### The HRMS spectra of 2



### The HRMS spectra of 3



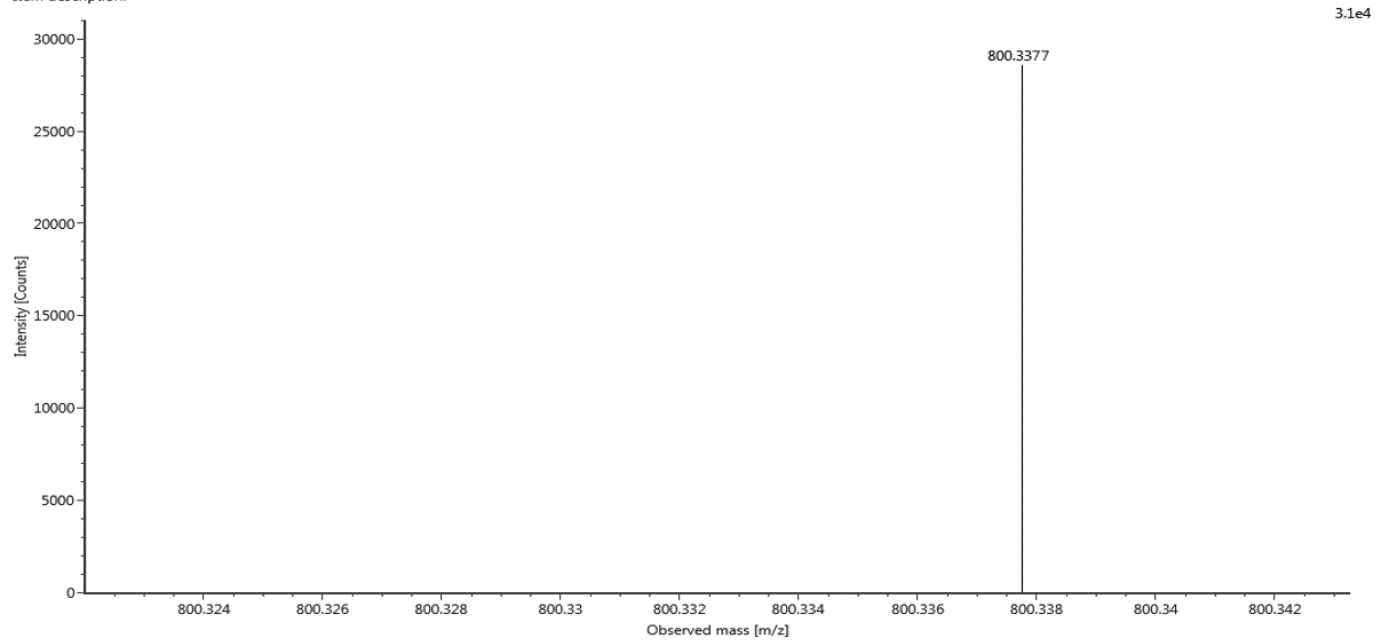
### The HRMS spectra of 4



# The HRMS spectra of 6

Item name: YXD-6  
Item description:

Channel name: 2: Average Time 0.1875 min : TOF MSe (50-2000) 6eV ESI+ : Centroided : Combined





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## Reference

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- [6] Li, L.; Hadt, R. G.; Yao, S.; Lo, W.-Y.; Cai, Z.; Wu, Q.; Pandit, B.; Chen, L. X.; Yu, L. *Chem. Mater.*, 2016, **28**, 5394-5399.
- [7] Kitamoto, K.; Sakai, K. *Chem. Commun.*, 2016, **52**, 1385-1388.
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- [9] G. Li, R. Song, W. Ma, X. Liu, Y. Li, B. Rao and G. He, *J. Mater. Chem. A*, 2020, **8**, 12278-12284.

## Author Contributions

Xiaodong Yang and Gang He conceived the idea for the study. Xiaodong Yang prepared the samples and conducted characterizations. Yueyan Zhang, Bingjie Zhang, Sikun Zhang, Xu Liu and Guoping Li helped to prepare and characterize the samples. Xiaodong Yang and Gang He contributed to the DFT calculations. Dake Chu, Yongtao Zhao discussed the manuscript. Xiaodong Yang and Gang He wrote the manuscript and all the authors revised and polished the manuscript.