

## Supporting Information

### **Photoswitchable Förster resonance energy transfer (FRET) within a heterometallic Ir-Pt macrocycle**

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## Section A. General information.

All reagents were of analytical purity and used without further treatment. TLC analyses were performed on silica-gel plates, and flash chromatography was conducted using silica-gel column packages. All air-sensitive reactions were carried out under argon atmosphere.  $^1\text{H}$  NMR,  $^{31}\text{P}$  NMR,  $^{19}\text{F}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker 400 MHz Spectrometer ( $^1\text{H}$ : 400 MHz;  $^{31}\text{P}$ : 161.9 MHz;  $^{19}\text{F}$ : 376 MHz;  $^{13}\text{C}$ : 100 MHz), Bruker 300 MHz Spectrometer ( $^1\text{H}$ : 300 MHz;  $^{31}\text{P}$ : 121.4 MHz;  $^{19}\text{F}$ : 282 MHz) or Bruker 500 MHz Spectrometer ( $^1\text{H}$ : 500 MHz;  $^{31}\text{P}$ : 202.3 MHz;  $^{13}\text{C}$ : 125 MHz) at 298 K. The  $^1\text{H}$  NMR chemical shifts are reported relative to residual solvent signals, and  $^{31}\text{P}$  NMR resonances are referenced to an internal standard sample of 85%  $\text{H}_3\text{PO}_4$  ( $\delta$  0.0). Coupling constants ( $J$ ) are denoted in Hz and chemical shifts ( $\delta$ ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. Electrospray ionization (ESI) mass spectra were recorded with a Waters Synapt G2 mass spectrometer. UV-vis spectra were recorded in a quartz cell (light path 10 mm) on a Shimadzu UV-Visible spectrophotometer. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Shimadzu fluorescence spectrophotometer. Quantum yields were measured using a Shimadzu fluorescence spectrophotometer with integrating sphere.

### Calculation of the efficiency of energy transfer $E$

The efficiency of energy transfer  $E$  can be calculated by the following equation<sup>S1</sup>:

$$E = 1 - F_{\text{PS}}/F_0$$

where  $F_{\text{PS}}$  is the fluorescence intensity of the chromophore at photostationary state (PSS) and  $F_0$  is its original fluorescence intensity before light irradiation.

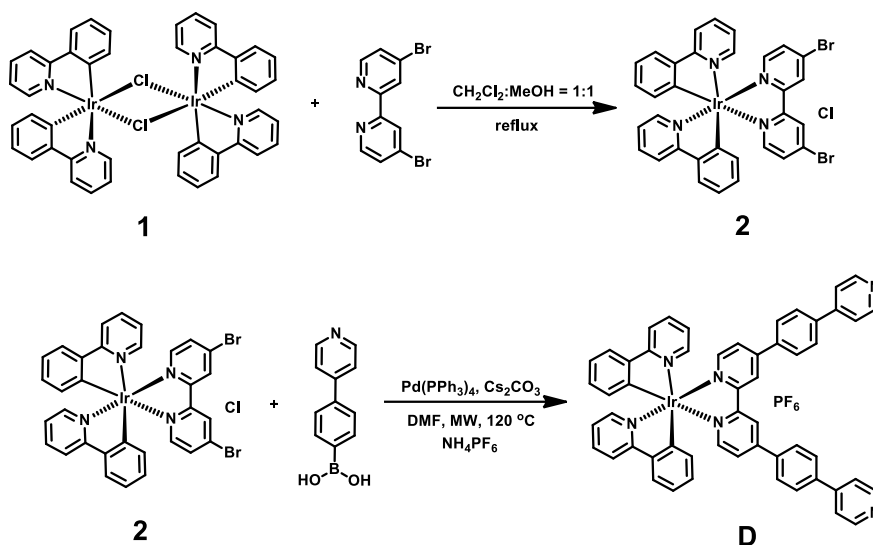
### Preparation of metallacycle **M** embedded PVDF film

0.35 g PVDF (polyvinylidene fluoride) was dissolved in 5.0 mL DMF to form a 70 mg/mL homogeneous solution. Then 1.4 mL of this solution was mixed with 2.0 mg metallacycle **M** in 0.2 mL acetone, followed by sonication of the mixture for 2.0 h to

form a homogeneous solution. The mixture was evenly smeared onto a quartz substrate and subsequently dried in the oven at 70 °C.

## Section B. Experimental Details for Synthesis and Characterization of New Compounds.

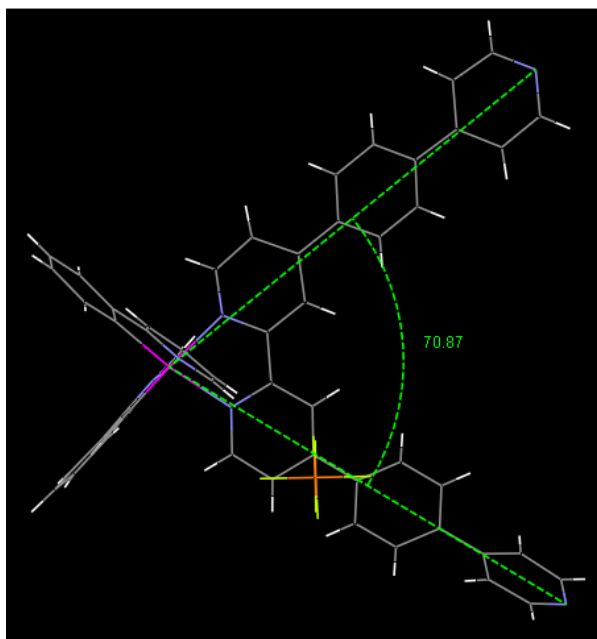
### 1. Synthesis of compound **D**.



Compound **1** was synthesized according to the literature<sup>S2</sup>. **1** (400 mg, 0.373 mmol), 4,4'-dibromo-2,2'-bipyridine (234 mg, 0.745 mmol, 2.0 eq.) were added to a solution of dichloromethane/methanol (40 mL, *v:v* = 1:1) and the mixture was stirred under reflux for 8.0 h. The organic solvent was evaporated and the resulting product was collected. The product was directly used in next step without further purification.

Compound **2** (500 mg, 0.588 mmol), 4-(pyridin-4-yl)phenylboronic acid (585 mg, 2.939 mmol, 5.0 eq.), Pd(PPh<sub>3</sub>)<sub>4</sub> (272 mg, 0.235 mmol, 0.4 eq.), Cs<sub>2</sub>CO<sub>3</sub> (1.910 g, 5.862 mmol, 10 eq.) were added to a 100 mL round flask and the flask was evacuated and refilled with N<sub>2</sub> three times. Then 40 mL degassed DMF was added and the mixture was heated in a microwave reactor at 120 °C for 2.0 h. Saturated NH<sub>4</sub>PF<sub>6</sub> solution was added and the precipitation was collected on Celite and washed with water. The residue was purified by column chromatography (dichloromethane:methanol = 20:1). The

product was collected and recrystallized from acetonitrile/diethyl ether to give an orange-red crystal (180 mg, 27%).  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz):  $\delta$  (ppm) = 9.48 (s, 2H), 8.72 (d,  $J$  = 6.0 Hz, 4H), 8.32 (d,  $J$  = 8.3 Hz, 2H), 8.26 (d,  $J$  = 8.2 Hz, 4H), 8.16 (d,  $J$  = 7.5 Hz, 2H), 8.10 (d,  $J$  = 8.5 Hz, 4H), 7.96 – 7.99 (m, 6H), 7.87 (d,  $J$  = 6.0 Hz, 4H), 7.81 (d,  $J$  = 5.7 Hz, 2H), 7.21 – 7.24 (m, 2H), 7.05 – 7.08 (m, 2H), 6.94 – 6.97 (m, 2H), 6.27 (d,  $J$  = 7.5 Hz, 2H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz):  $\delta$  (ppm) = 167.36, 156.57, 151.26, 150.76, 150.50, 149.72, 149.61, 146.38, 144.36, 139.51, 139.32, 136.49, 131.58, 130.81, 129.10, 128.14, 126.41, 125.63, 124.53, 123.07, 122.83, 121.81, 120.59. ESI-MS:  $m/z$  calcd for  $\text{C}_{54}\text{H}_{38}\text{IrN}_6([\text{M} - \text{PF}_6]^+)$ : 963.14, found: 963.30.

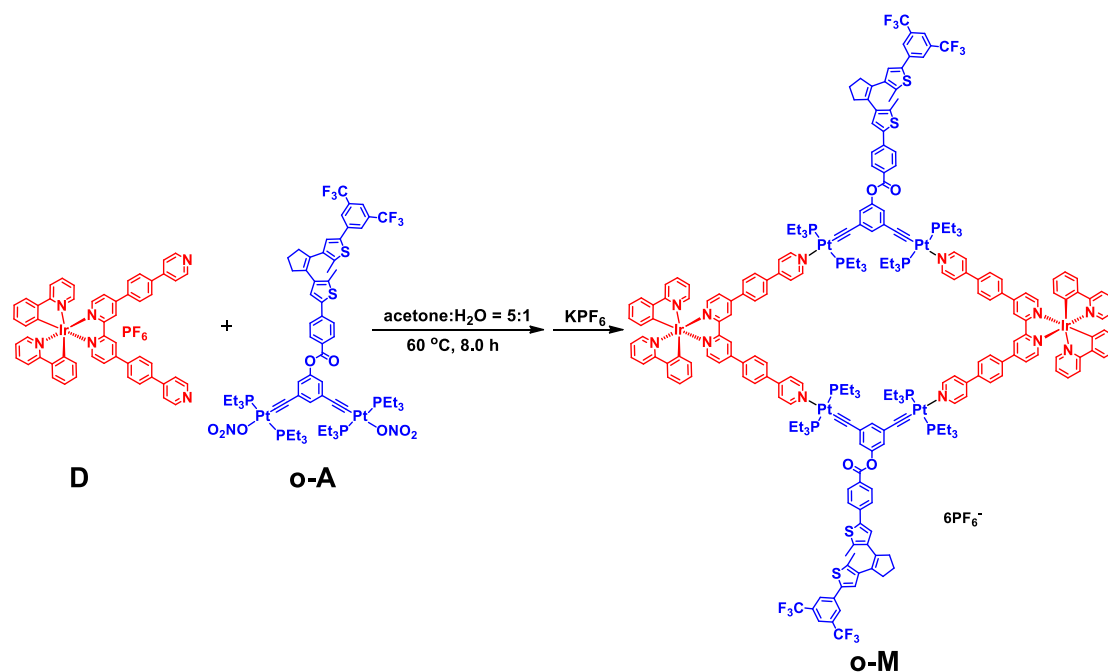


**Figure S1.** Crystal structure of ligand **D**. The angle between N-Ir-N was 70.87°.

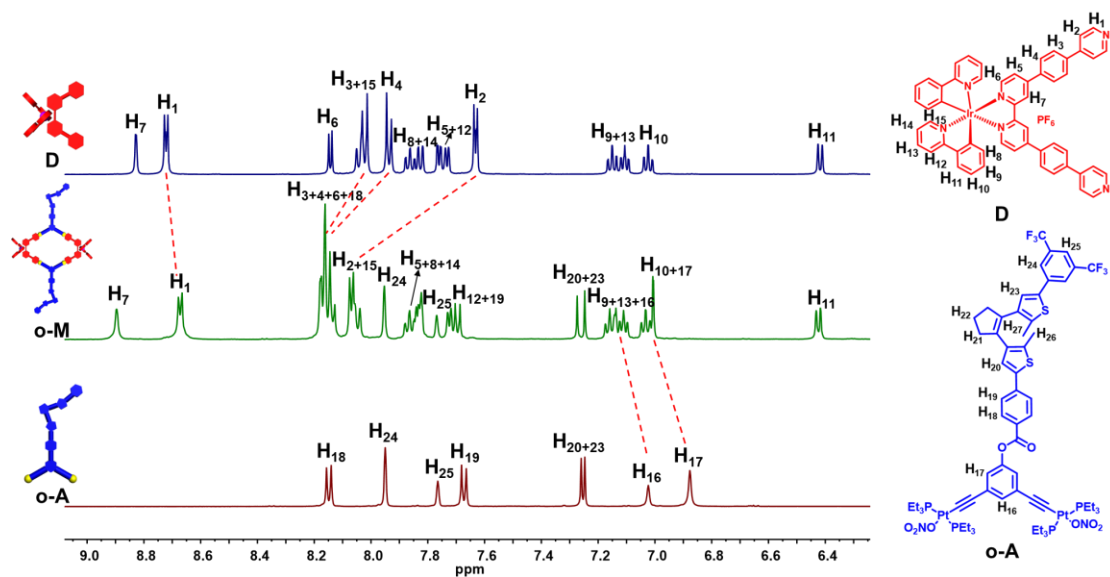
**Table S1.** Crystal data and structure refinement parameters for ligand **D**.

Identification code	exp_657
CCDC number	1920587
Empirical formula	C <sub>54</sub> H <sub>38</sub> F <sub>6</sub> IrN <sub>6</sub> P
Formula weight	1108.07
Temperature/K	99.9(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	14.3137(2)
b/Å	25.3773(2)
c/Å	14.51620(10)
α/°	90
β/°	106.3360(10)
γ/°	90
Volume/Å <sup>3</sup>	5060.03(9)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.455
μ/mm <sup>-1</sup>	5.943
F(000)	2200.0
Crystal size/mm <sup>3</sup>	0.48 × 0.36 × 0.32
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.318 to 149.404
Index ranges	-17 ≤ h ≤ 16, -31 ≤ k ≤ 31, -18 ≤ l ≤ 18
Reflections collected	134662
Independent reflections	10215 [R <sub>int</sub> = 0.0826, R <sub>sigma</sub> = 0.0329]
Data/restraints/parameters	10215/0/613
Goodness-of-fit on F <sup>2</sup>	1.114
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0641, wR <sub>2</sub> = 0.1497
Final R indexes [all data]	R <sub>1</sub> = 0.0681, wR <sub>2</sub> = 0.1522
Largest diff. peak/hole / e Å <sup>-3</sup>	1.88/-1.46

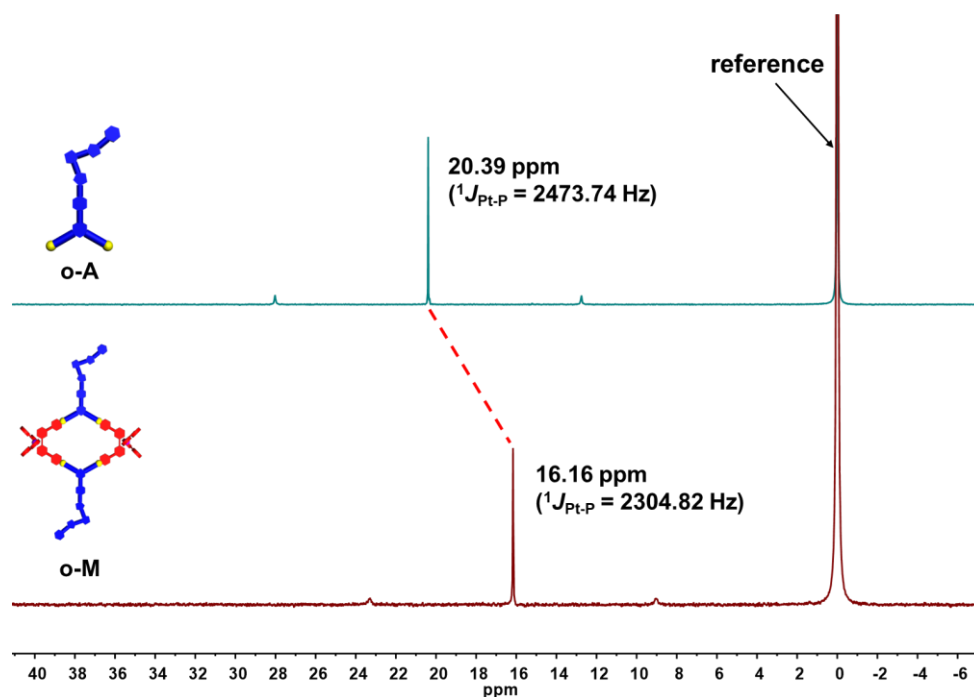
## 2. Synthesis of heterometallic Ir-Pt macrocycle **o-M**.



Compound **o-A** was synthesized according to the literature<sup>S3</sup>. The dipyriddy donor ligand **D** (4.00 mg, 3.61 μmol) and the diplatinum 120° acceptor **o-A** (6.14 mg, 3.61 μmol) were weighed accurately into a glass vial away from light. To the vial was added 1.5 mL acetone and 0.3 mL water, and the reaction solution was then stirred in the dark place at 60 °C for 8.0 h to yield a homogeneous solution. After cooling to room temperature, KPF<sub>6</sub> was added to form a precipitate, then the precipitate was washed with water for three times and dried under vacuum. Mp: >300 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz): δ (ppm) = 8.90 (s, 2H), 8.68 (d, *J* = 7.0 Hz, 4H), 8.13 – 8.18 (m, 12H), 8.04 – 8.08 (m, 6H), 7.95 (s, 2H), 7.82 – 7.88 (m, 6H), 7.77 (s, 1H), 7.69 – 7.73 (m, 4H), 7.27 (s, 1H), 7.25 (s, 1H), 7.10 – 7.17 (m, 5H), 7.01 – 7.05 (m, 4H), 6.43 (d, *J* = 7.5 Hz, 2H), 2.91 – 2.94 (m, 4H), 2.11 – 2.20 (m, 8H), 1.86 – 1.89 (m, 24H), 1.22 – 1.28 (m, 36H). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 202 MHz): δ (ppm) = 16.16 (<sup>1</sup>*J*<sub>Pt-P</sub> = 2304.82 Hz). MS (ESI-MS): *m/z* calcd for [M – 5PF<sub>6</sub><sup>-</sup>]<sup>5+</sup>: 1045.26, found: 1045.21; *m/z* calcd for [M – 4PF<sub>6</sub><sup>-</sup>]<sup>4+</sup>: 1342.82, found: 1342.75.

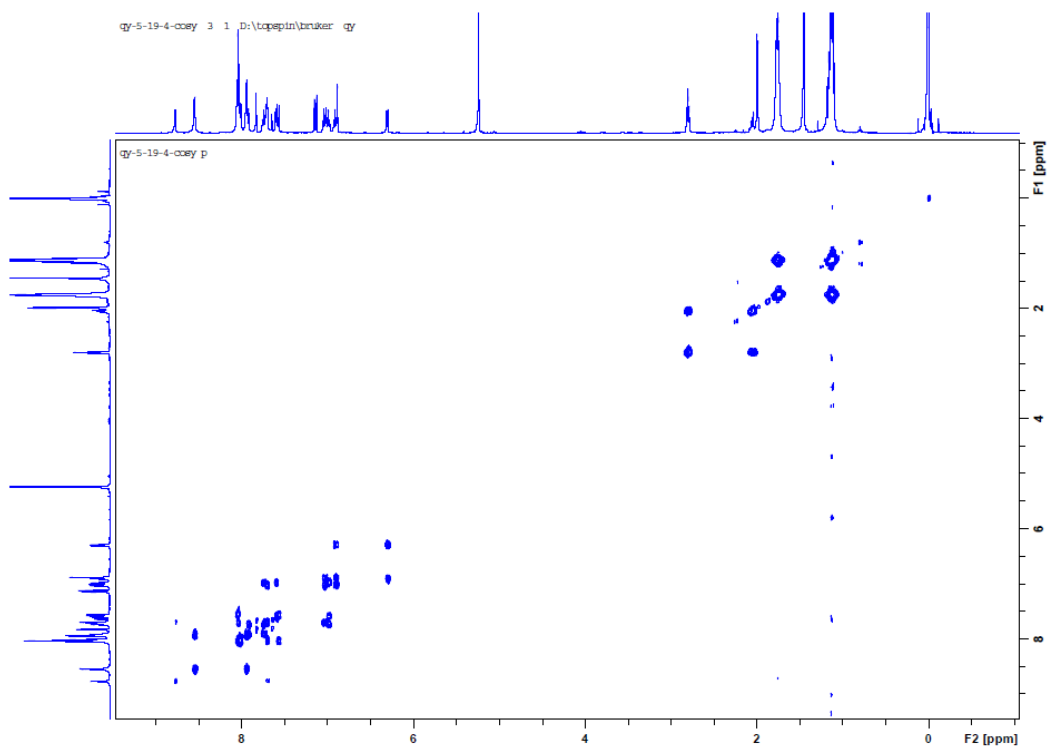


**Figure S2.** The partial  $^1\text{H}$  NMR spectra (500 MHz, 298 K) of acceptor **o-A**, dipyrindine donor **D**, and their corresponding self-assembled heterometallic Ir-Pt macrocycle **o-M** in  $\text{CD}_2\text{Cl}_2$ .

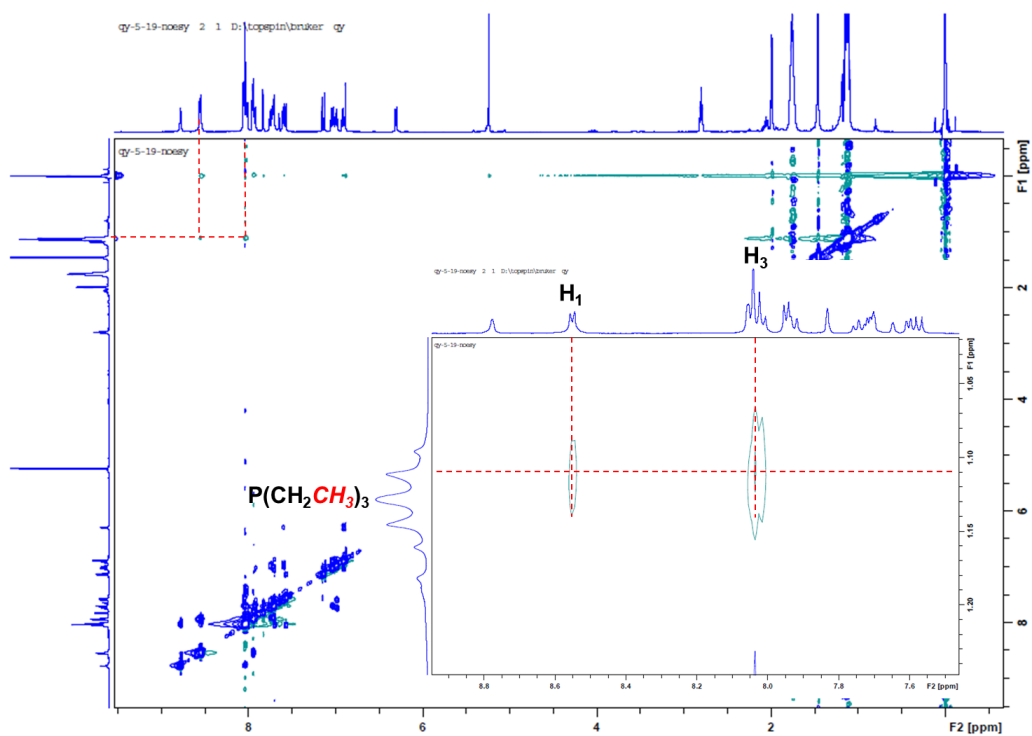


**Figure S3.** The  $^{31}\text{P}$  NMR spectra (162 MHz, 298 K) of acceptor **o-A**, and their corresponding self-assembled heterometallic Ir-Pt macrocycle **o-M** in  $\text{CD}_2\text{Cl}_2$ .

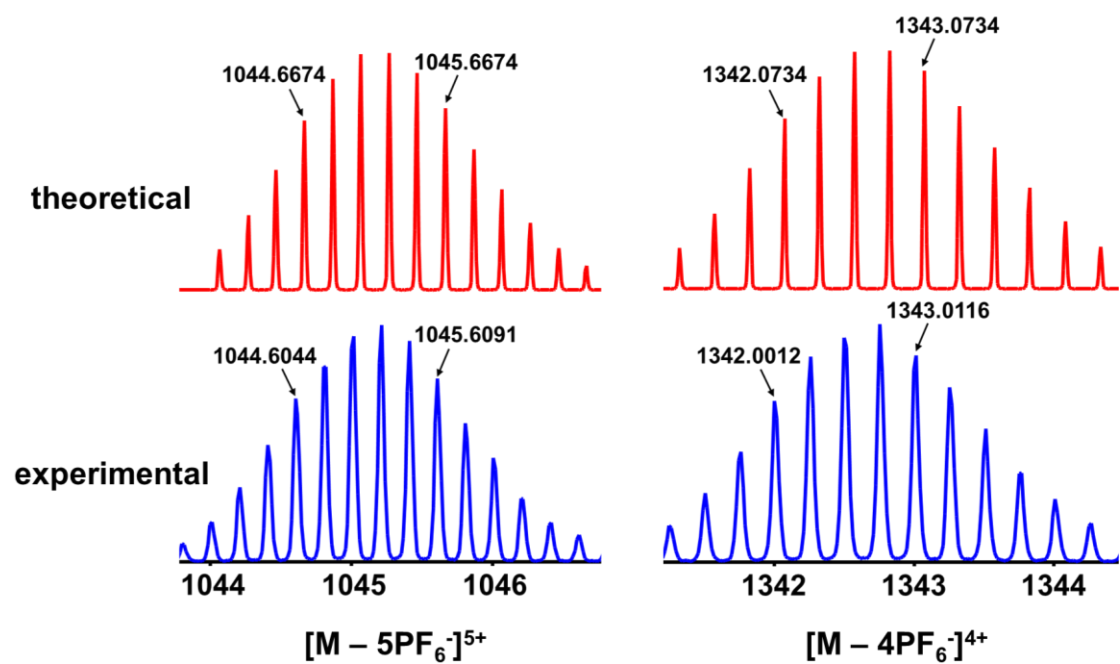




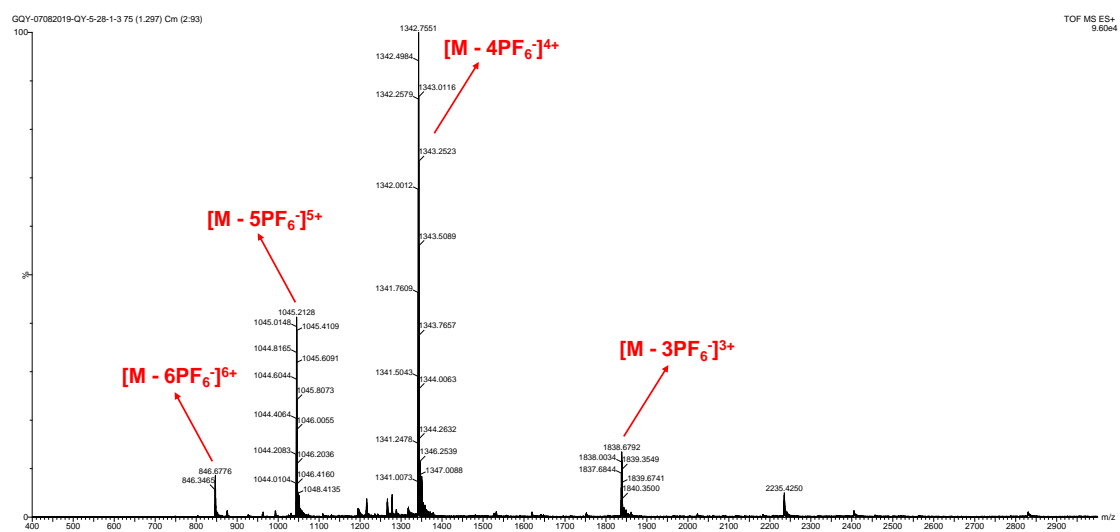
**Figure S4.** 2D COSY NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **o-M**.



**Figure S5.** 2D NOESY NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of **o-M**. (The signals in the insert photographs indicated the formation of Pt-N bonds).

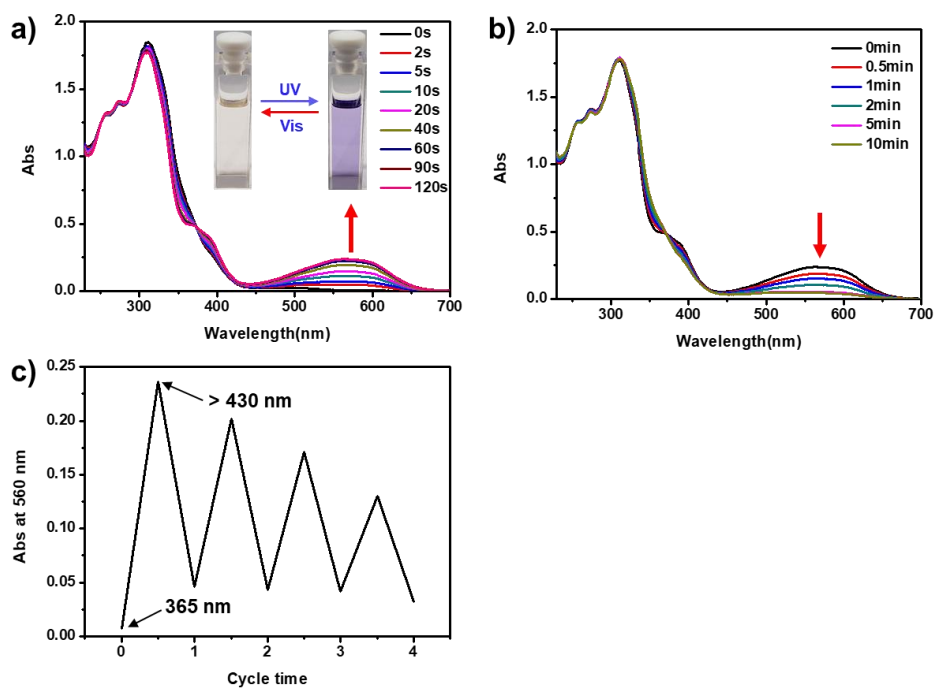


**Figure S6.** ESI-TOF-MS spectrum of *o*-M. Theoretical (top) and experimental (bottom) isotopic distribution.

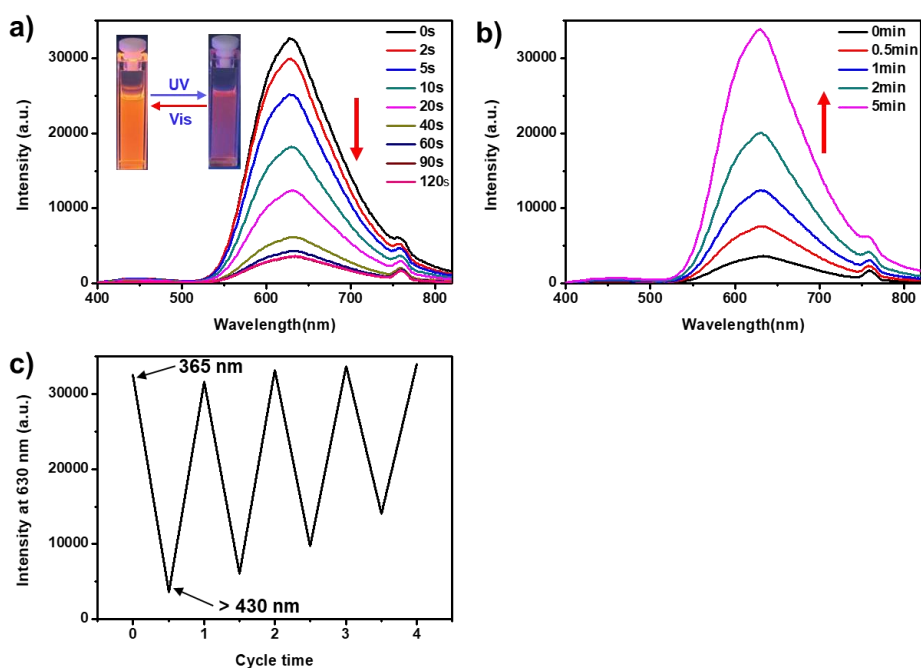


**Figure S7.** ESI-MS for *o*-M.

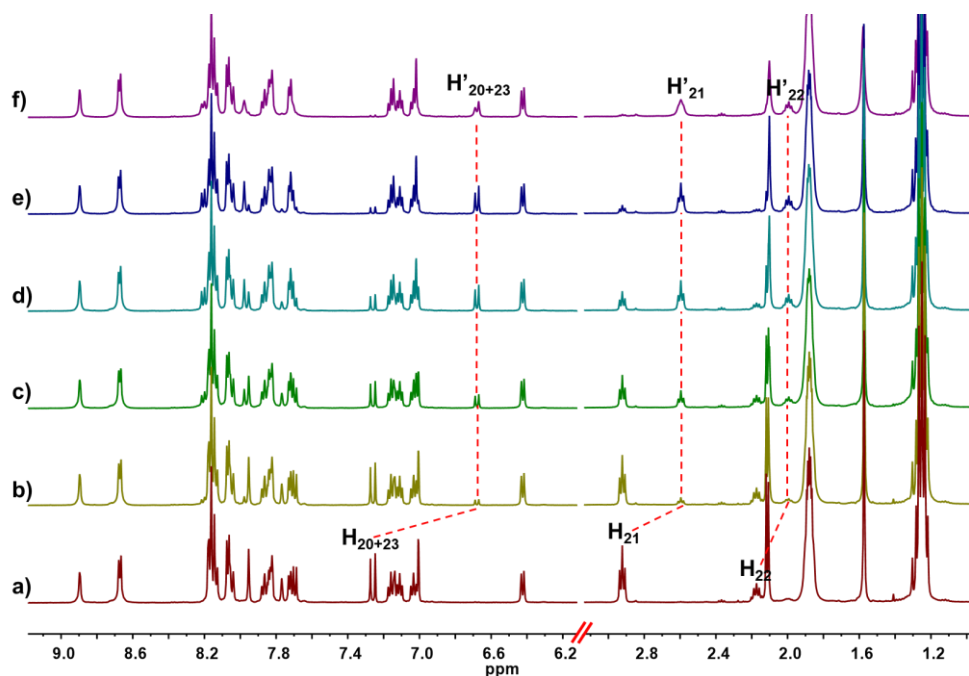
## Section C. Photochromism Studies of Metallacycle **M**.



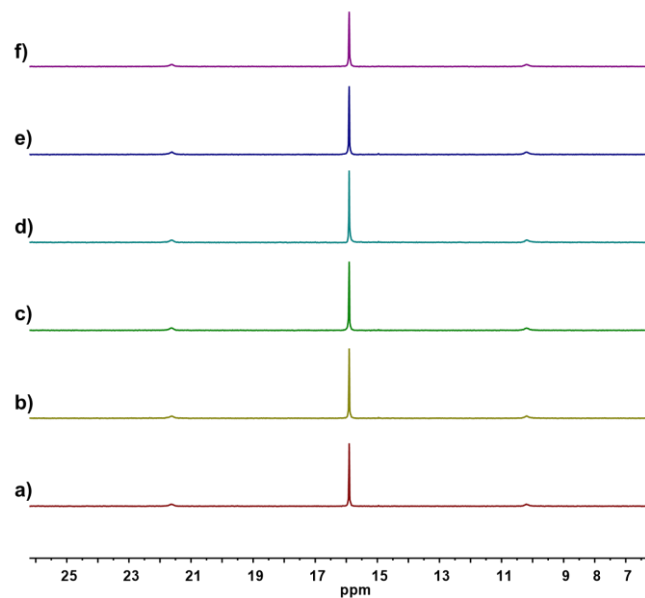
**Figure S8.** (a) Absorption spectral changes of metallacycle **M** ( $1.6 \times 10^{-5}$  mol/L in CH<sub>2</sub>Cl<sub>2</sub>) under irradiation at 365 nm in air. (b) Absorption spectral changes of metallacycle **M** ( $1.6 \times 10^{-5}$  mol/L in CH<sub>2</sub>Cl<sub>2</sub>) under visible light (>430 nm) in air. (c) Fatigue resistance of metallacycle **M** ( $1.6 \times 10^{-5}$  mol/L in CH<sub>2</sub>Cl<sub>2</sub>) upon alternating UV (365 nm) and visible light (>430 nm) irradiation in air.



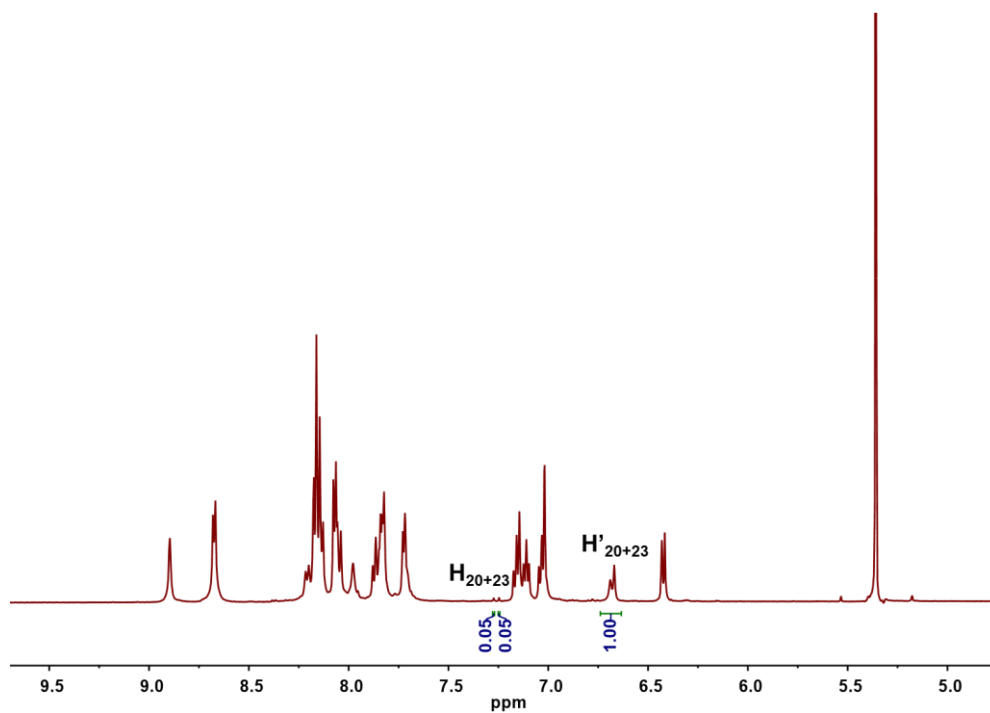
**Figure S9.** (a) Emission spectra changes of metallacycle **M** ( $1.6 \times 10^{-5}$  mol/L in  $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{ex}} = 380$  nm) under irradiation at 365 nm in air. (b) Emission spectra changes of metallacycle **M** ( $1.6 \times 10^{-5}$  mol/L in  $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{ex}} = 380$  nm) under irradiation with visible light ( $>430$  nm) in air. (c) Changes in emission intensity of metallacycle **M** at 630 nm over few cycles of photoisomerization. ( $1.6 \times 10^{-5}$  mol/L in  $\text{CH}_2\text{Cl}_2$ ,  $\lambda_{\text{ex}} = 380$  nm) in air.



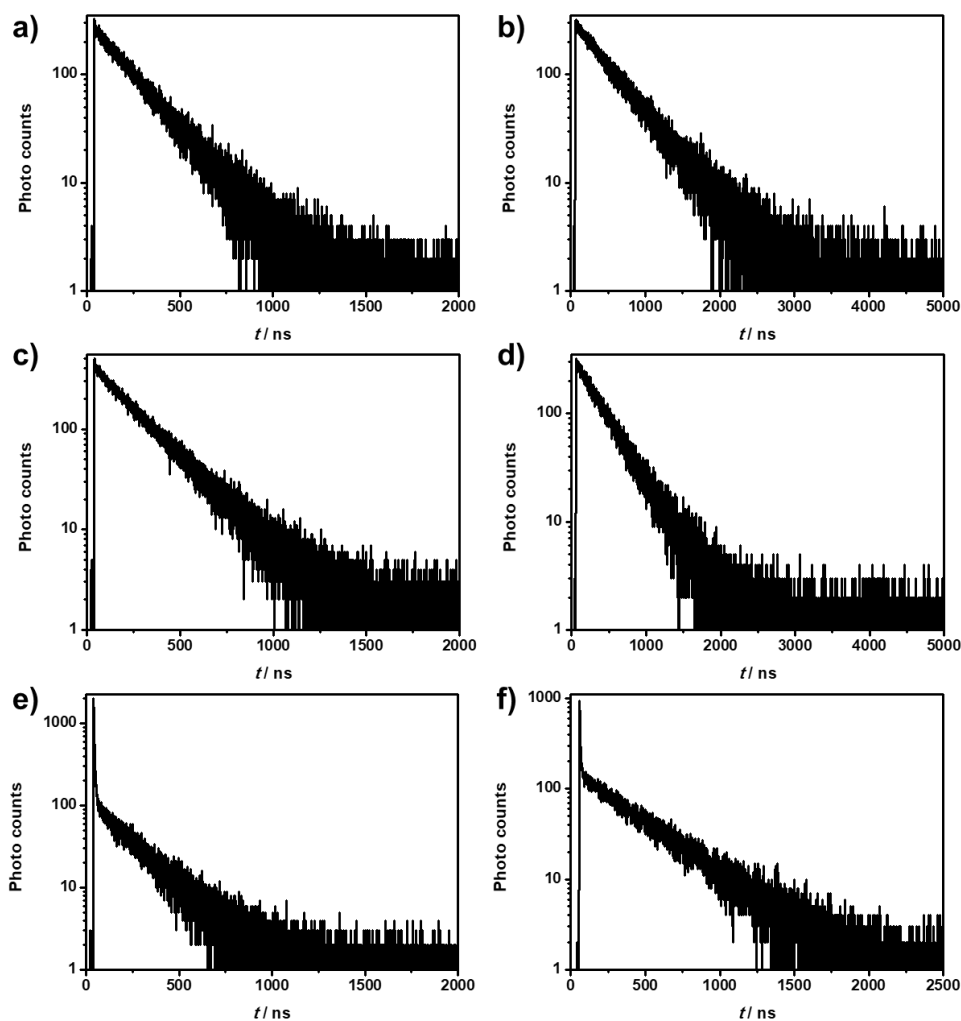
**Figure S10.** Partial  $^1\text{H}$  NMR spectra of structural transformation of metallacycle **M** from ring-open to ring-closed form (500MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K): (a) before irradiation; (b-f) after irradiation at 365 nm for (b) 5; (c) 15; (d) 35; (e) 60; (f) 120 min.



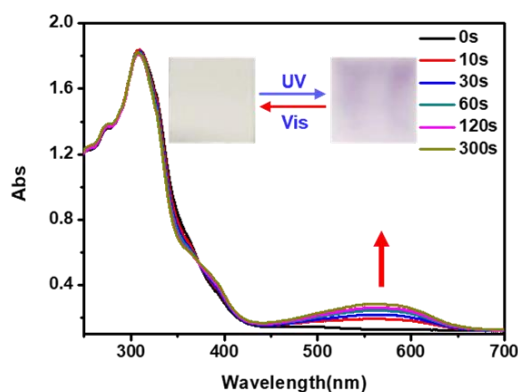
**Figure S11.**  $^{31}\text{P}$  NMR spectra of structural transformation of metallacycle **M** from ring-open to ring-closed form (202MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K): (a) before irradiation; (b-e) after irradiation at 365 nm for (b) 5; (c) 15; (d) 35; (e) 60; (f) 120 min.



**Figure S12.**  $^1\text{H}$  NMR indicates that nearly 91% of metallacycle **M** is in the ring-closed form (**c-M**) at the photostationary state ( $\text{PSS}_{365\text{nm}}$ ).



**Figure S13.** Emission lifetime measurements of (a) **D** in air, (b) **D** in  $N_2$ , (c) **o-M** in air, (d) **o-M** in  $N_2$ , (e) **c-M** in air and (f) **c-M** in  $N_2$  in  $CH_2Cl_2$ . The lifetime of **c-M** follows a double-exponential decay. The short lifetime indicated that the emission of Ir complex unit was effectively quenched by the ring-closed isomer of the diarylethene (**c-A**) moiety through FRET effect. Moreover, the long lifetime might be due to the residual small amount of ring-open isomer of the diarylethene (**o-A**) in the solution.

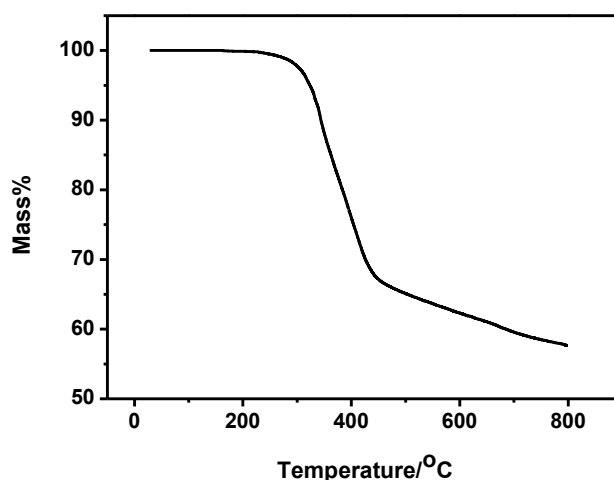


**Figure S14.** Absorption spectral changes of a PVDF film loaded with metallacycle **o-M** (2.0 wt%) under irradiation at 365 nm.

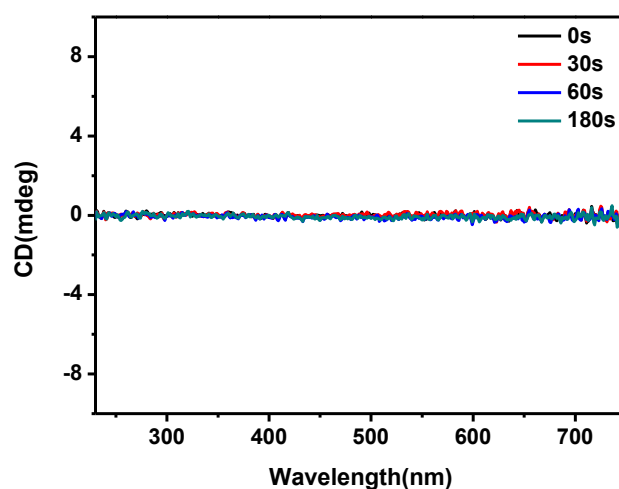
**Table S2.** Quantum yields of the PVDF film loaded with **o-M** or **c-M**.

	$\Phi_F/\%$
<b>o-M</b> in PVDF	2.38
<b>c-M</b> in PVDF	0.04

The emission quantum yields of **o-M** and **c-M** in PVDF film were found to be lower than that in the solution, which is probably due to the aggregation induced quenching effect of the metallacycle in the solid state<sup>S4</sup>.

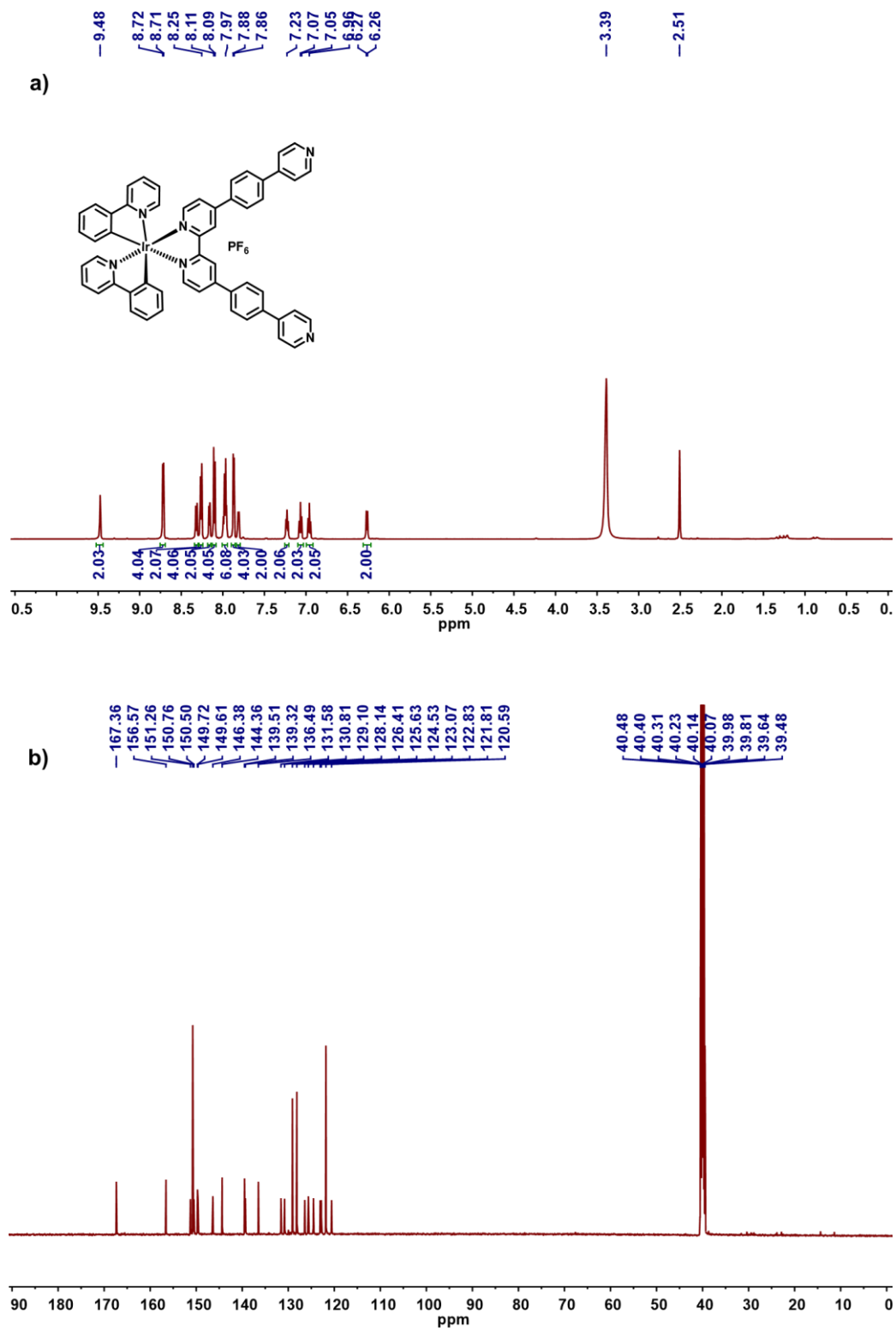


**Figure S15.** Thermogravimetric (TG) curves of metallacycle **o-M**, which showed no obvious decomposition before 300 °C. This observation indicated that no thermal decomposition occurred during the drying process of metallacycle **o-M** embedded PVDF film (70 °C).



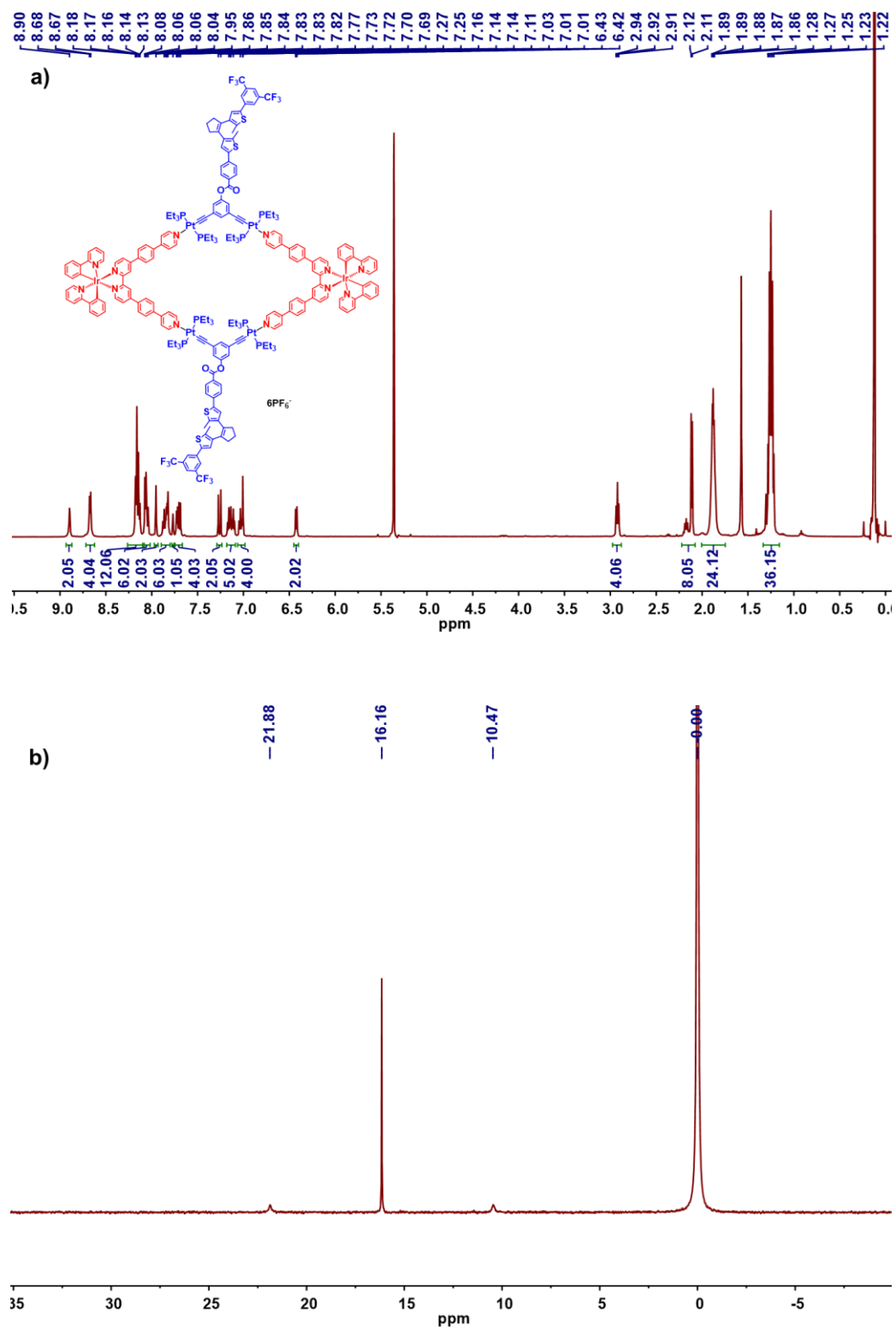
**Figure S16.** CD spectra of metallacycle **M** ( $1.6 \times 10^{-5}$  mol/L in  $\text{CH}_2\text{Cl}_2$ ) before and after irradiation at 365 nm. No obvious CD signal was found before and after UV irradiation, which indicated that both the Ir complex and ring-closed diarylethene moiety were racemic in this system.

## Section D. The Copy of $^1\text{H}$ , $^{31}\text{P}$ , $^{13}\text{C}$ NMR, and MS Spectra of New Compounds.

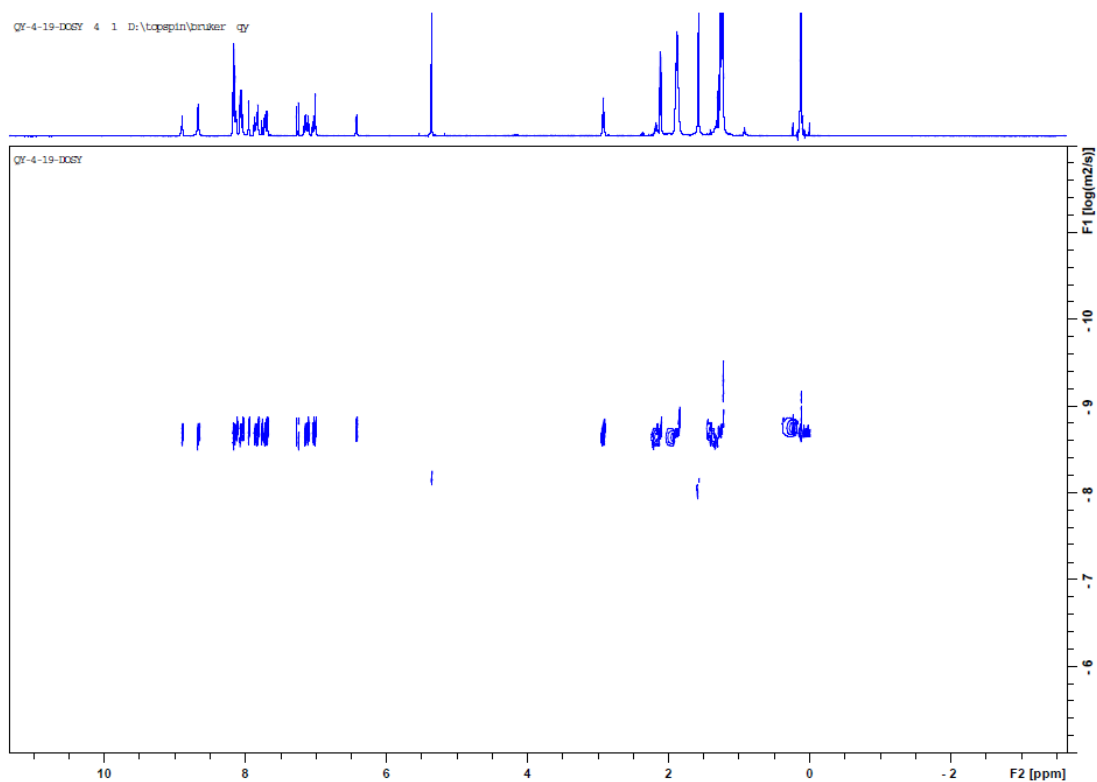


**Figure S17.** (a)  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{DMSO-}d_6$ , 298 K) and (b)  $^{13}\text{C}$  NMR spectrum (125 MHz,  $\text{DMSO-}d_6$ , 298 K) of compound **D**.

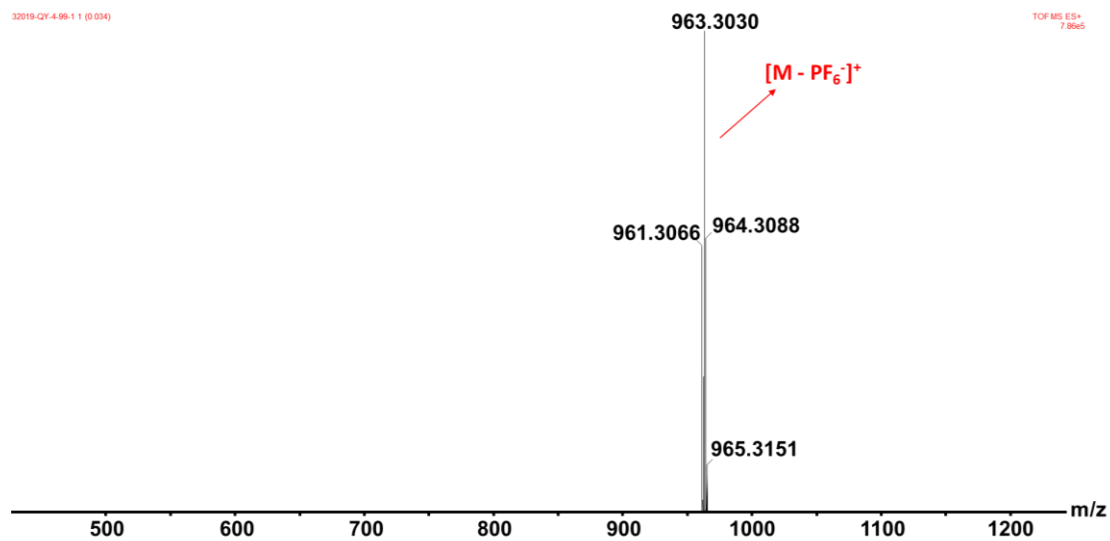




**Figure S18.** (a)  $^1\text{H}$  NMR spectrum (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) and (b)  $^{31}\text{P}$  NMR spectrum (202 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of metallacycle **o-M**.



**Figure S19.** 2D DOSY NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) spectrum of metallacycle **o-M**.



**Figure S20.** ESI-MS for compound **D**.

## Section E. References.

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- S2. L.-J. Liu, W. Wang, S.-Y. Huang, Y. Hong, G. Li, S. Lin, J. Tian, Z. Cai, H.-M. D. Wang, D.-L. Ma and C.-H. Leung, *Chem. Sci.*, 2017, **8**, 4756–4763.
- S3. Y. Qin, L.-J. Chen, F. Dong, S.-T. Jiang, G.-Q. Yin, X. Li, Y. Tian and H.-B. Yang, *J. Am. Chem. Soc.*, 2019, **141**, 8943–8950.
- S4. J. B. Birks, *Photophysics of Aromatic Molecules*; Wiley: New York, 1970.