Electronic Supplementary Information (ESI) for

Effects of Fused Rings Linked to the 2,5-Position of Pyrrole Derivatives with Near-Infrared Emission on their Aggregation-Enhanced Emission Properties

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1. Experimental

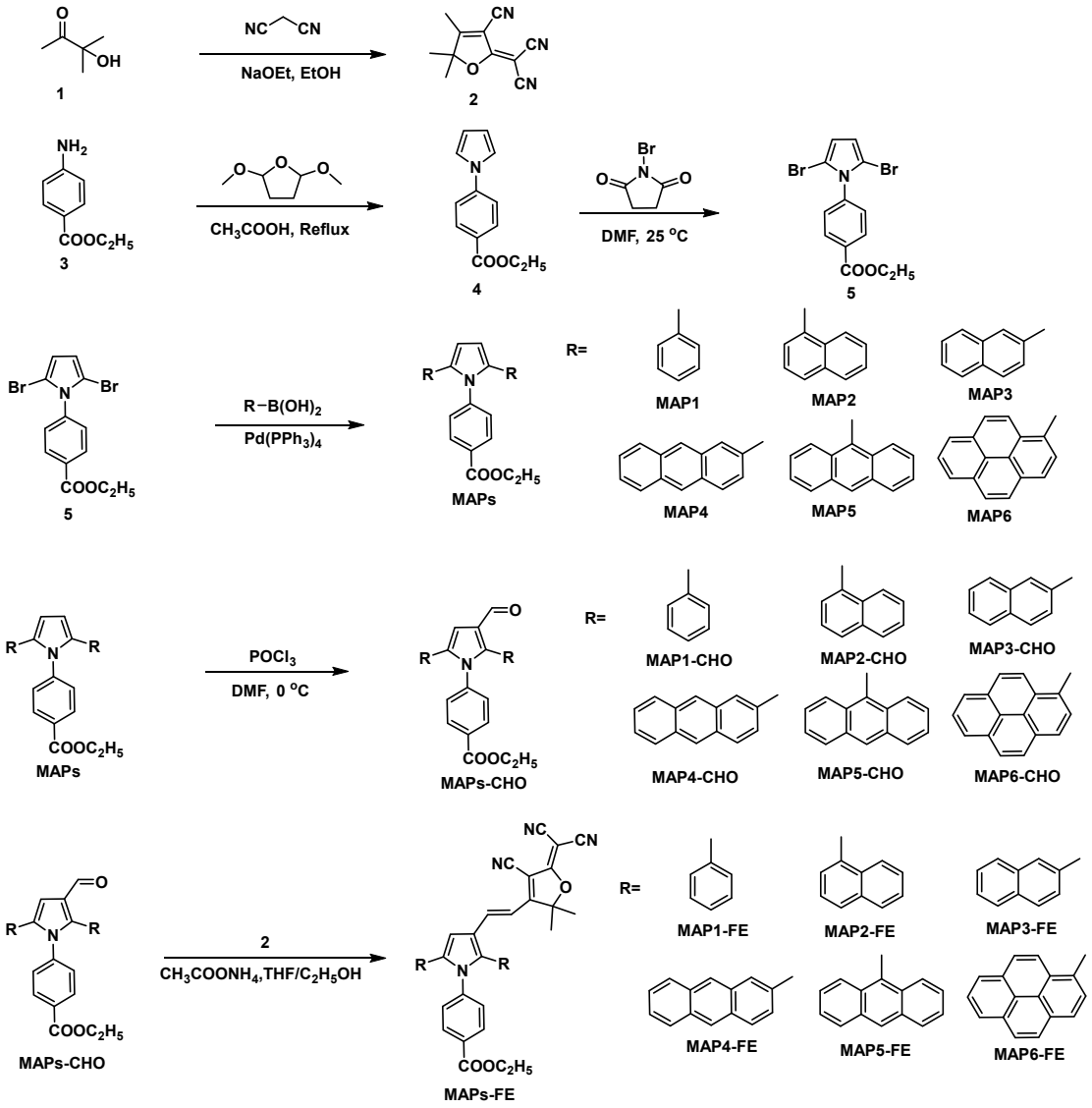
1.1 Materials

The target compounds were obtained by conventional synthetic routes, as shown in Scheme S1. All chemicals were used from commercial suppliers without further purification unless otherwise stated. CuCl, $Pd(PPh_3)_4$ and ethyl 4-aminobenzoate **3** were purchased from J&K. $POCl_3$ was purchased from Xiya Reagent. 3-Hydroxy-3-methylbutan-2-one, malononitrile, 2,5-dimethoxytetrahydrofuran, naphthalen-1-ylboronic acid, naphthalen-2-ylboronic acid, and 1-bromopyrrolidine-2,5-dione were purchased from Energy Chemical. Anthracen-2-ylboronic acid and anthracen-9-ylboronic acid were purchased from Bidepharm. Pyren-1-ylboronic acid was purchased from Alfa. Chloroform-*d* and DMSO-d_6 were purchased from Innochem.

1.2 Equipment

^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer. Mass spectra were collected by using a Finnigan Biflex III mass spectrometer. UV-Vis spectra were recorded on a TU-1901 double beam UV-Vis spectrophotometer. Fluorescence spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer. PL quantum yields were measured by using an integrating sphere on a NanoLog FL3-2iHR fluorescence spectrometer (Horiba Jobin Yvon), and PL time-resolved decays were measured with a DeltaFlex ultrafast lifetime spectrofluorometer (Horiba Jobin Yvon). Single-crystal data were collected on a Bruker-AXS SMART APEX 2 CCD diffractometer.

1.3 Synthesis



Scheme S1. Synthetic route to target compounds.

The compound 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile **2** was prepared by a method in the literature that has been reported.[1] The compounds ethyl 4-(1*H*-pyrrol-1-yl)benzoate **4**, ethyl 4-(2,5-dibromo-1*H*-pyrrol-1-yl)benzoate **5**, **MAP1**, and **MAP1-CHO** were prepared according to the synthetic route shown in Scheme S1. Details can be found in our previous work.[2] The synthesis and characterization of the other target compounds are given below.

Synthesis of ethyl 4-(2,5-di(naphthalen-1-yl)-1*H*-pyrrol-1-yl)benzoate (MAP2). 4-(2,5-Dibromo-1*H*-pyrrol-1-yl)benzoate (0.3729 g, 1.00 mmol), naphthalen-1-ylboronic

acid (0.5126 g, 3.00 mmol) and $Pd(PPh_3)_4$ (0.0462 g, 0.04 mmol) were dissolved in degassed DMF (10 ml), and then a saturated aqueous solution of K_2CO_3 (3 mL) was added. After stirring for 24 h at 90 °C under nitrogen protection, the solution was cooled to room temperature and then extracted with dichloromethane and washed with water. Then, the organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography using a dichloromethane/petroleum ether mixture (1/5, V_d/V_p) as the eluent to give compound **MAP2** with 49.7% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, *J* = 8.0 Hz, 2H), 7.86-7.78 (m, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.51-7.40 (m, 6H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.65 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.83, 142.83, 133.59, 133.03, 132.56, 130.96, 129.39, 129.24, 128.16, 127.96, 127.92, 127.21, 126.17, 125.80, 124.93, 112.33, 60.88, 14.14. MS (MALDI, *m/z*) Calcd for $C_{33}H_{25}NO_2$ $[M]^+$: 467.19, found: 466.94.

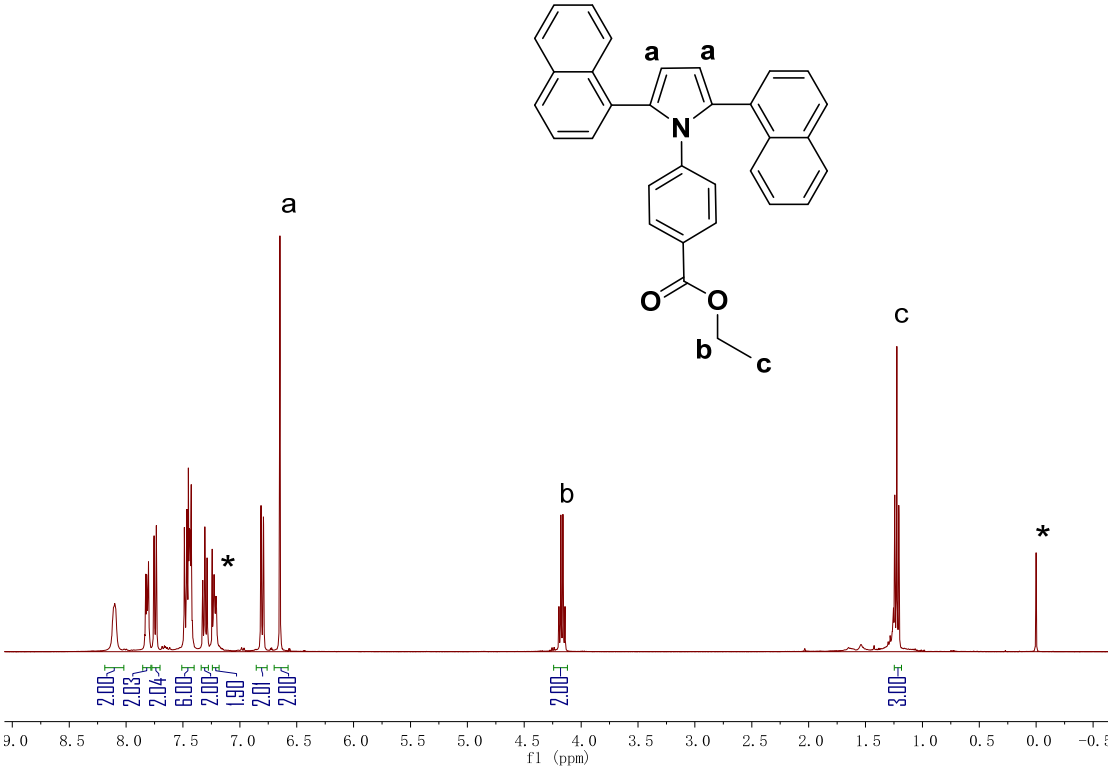


Figure S1. ^{1}H NMR spectrum of **MAP2** in $CDCl_3$.

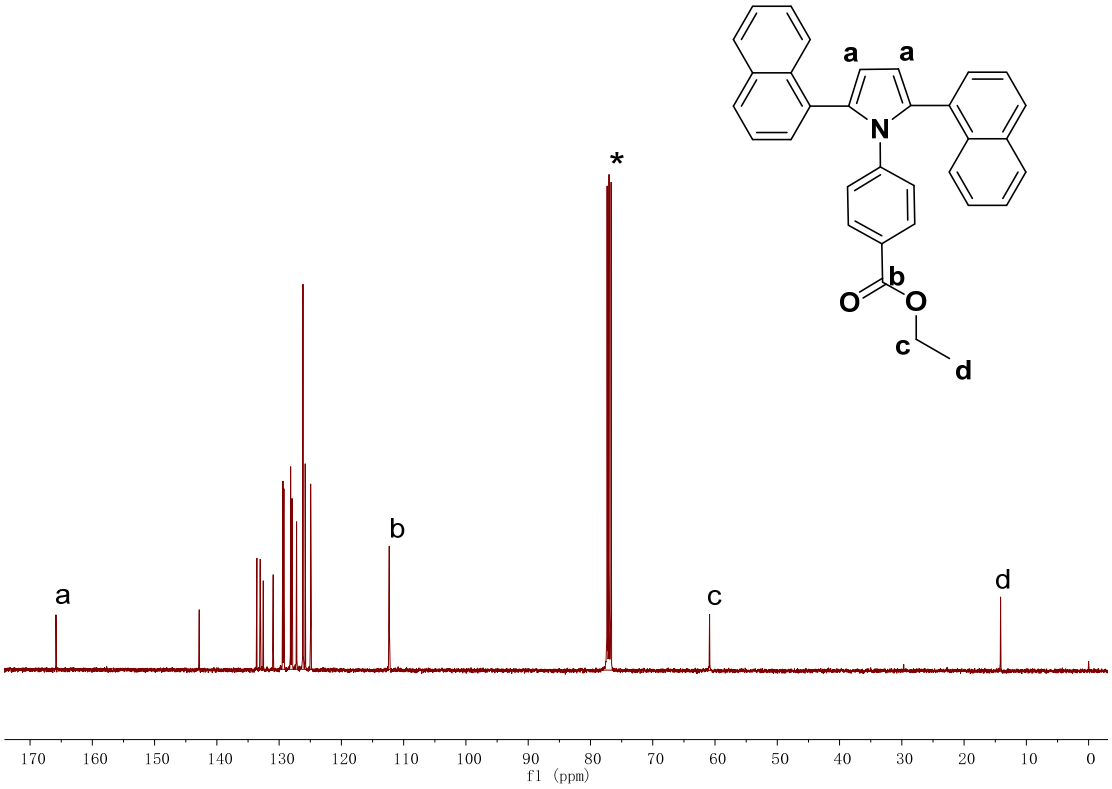


Figure S2. ^{13}C NMR spectrum of **MAP2** in $CDCl_3$.

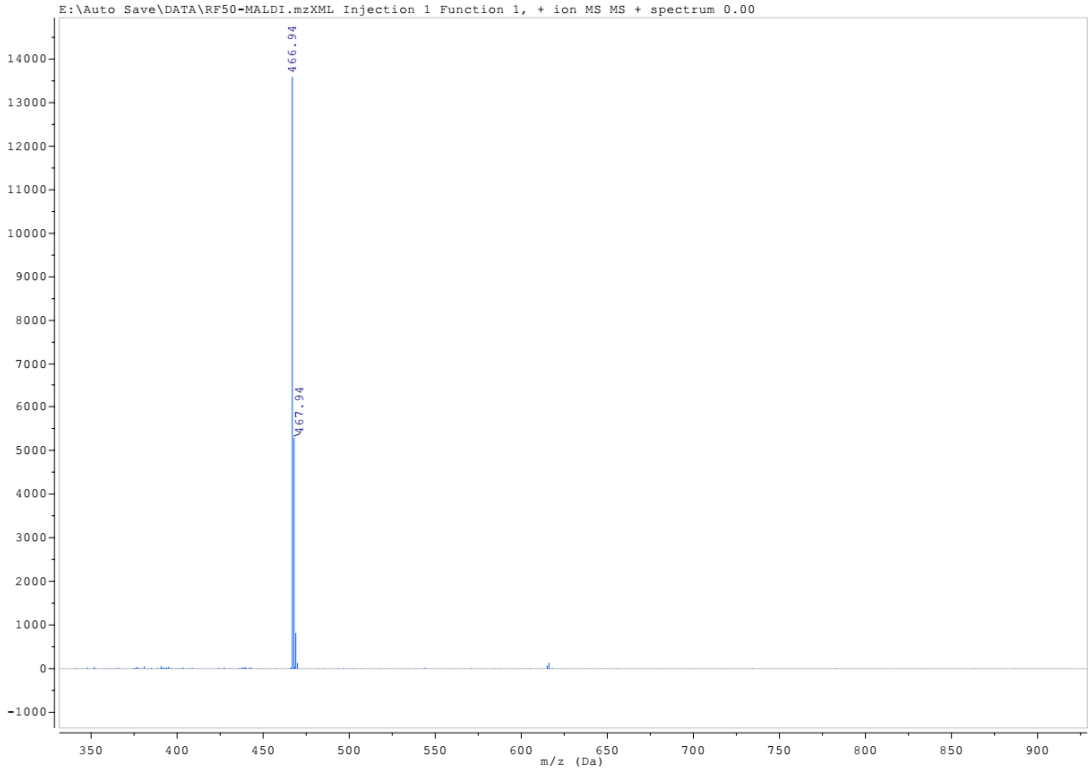


Figure S3. MS spectrum of **MAP2**.

Synthesis of ethyl 4-(2,5-di(naphthalen-2-yl)-1*H*-pyrrol-1-yl)benzoate (MAP3). The synthesis procedure is the same as that of **MAP2**, and only replaced naphthalen-1-ylboronic acid by naphthalen-2-ylboronic acid (0.5126 g, 3.00 mmol). The yield of **MAP2** gives 74.4%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.4 Hz, 2H), 7.78-7.72 (m, 2H), 7.69-7.58 (m, 6H), 7.46-7.37 (m, 4H),7.15 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.65 (s, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.94, 142.95, 135.94, 133.24, 131.92, 130.40, 130.26, 129.08, 128.74, 127.98, 127.59, 127.52, 127.48, 126.98, 126.23, 125.92, 111.33, 61.21, 14.28. MS (MALDI, *m/z*) Calcd for $C_{33}H_{25}NO_2$ $[M]^+$: 467.19, found: 466.98.

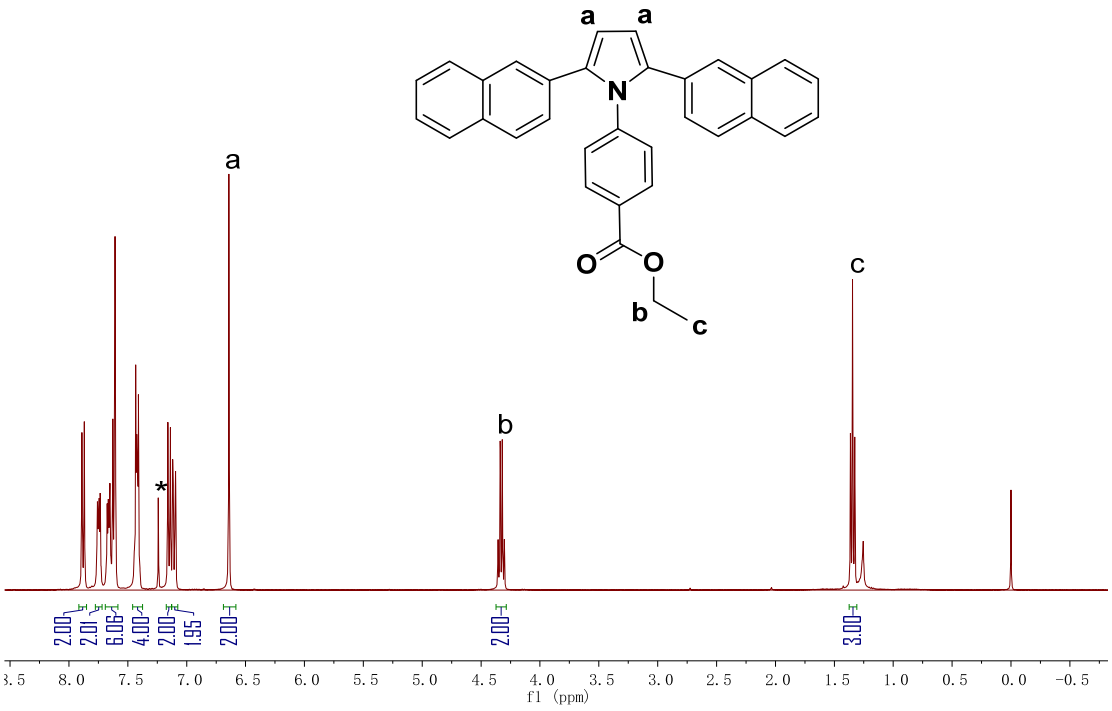


Figure S4. ^{1}H NMR spectrum of **MAP3** in $CDCl_3$.

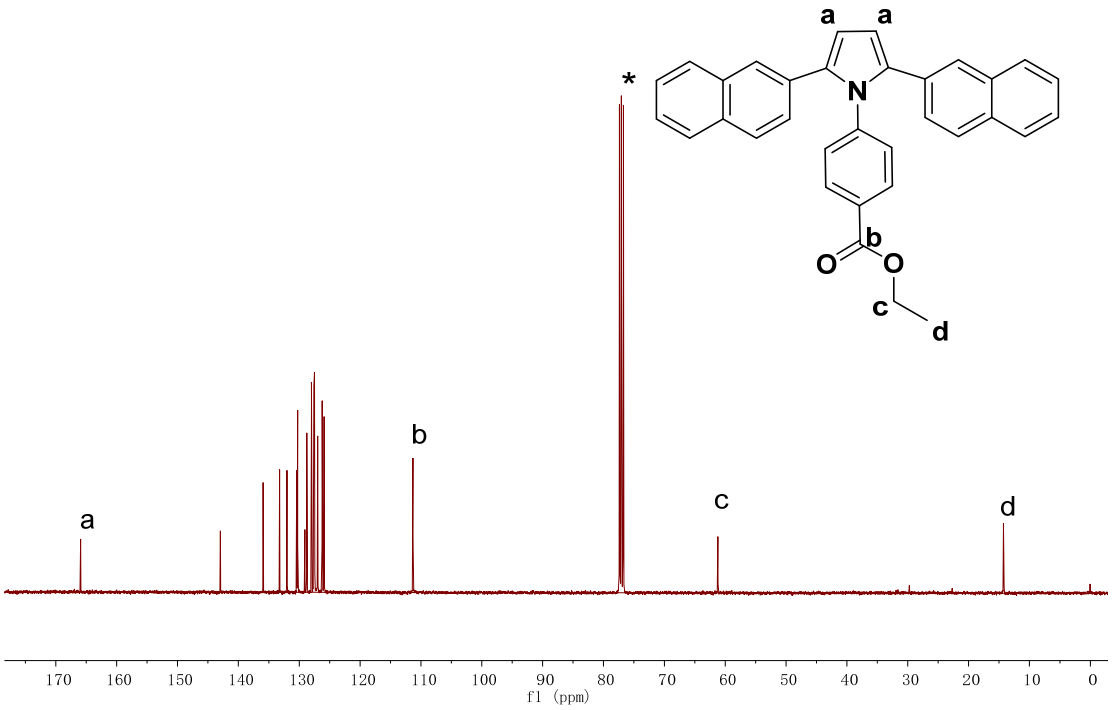


Figure S5. ^{13}C NMR spectrum of **MAP3** in $CDCl_3$.

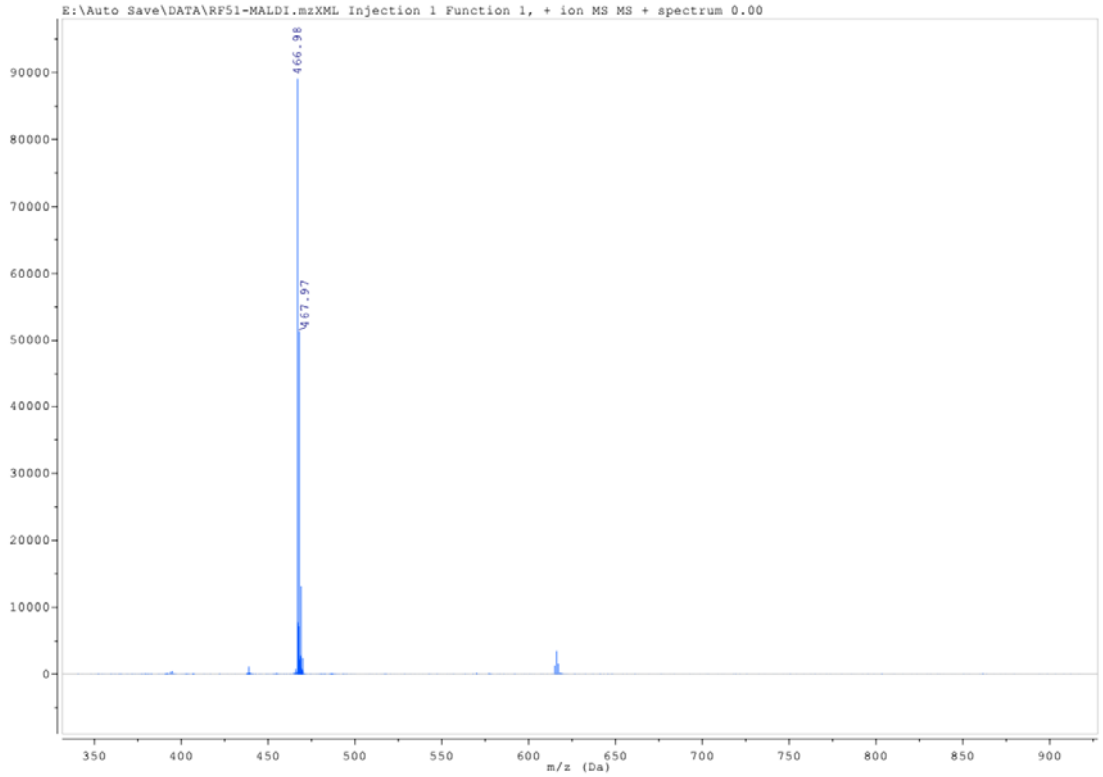


Figure S6. MS spectrum of **MAP3**.

Synthesis of ethyl 4-(2,5-di(anthracen-2-yl)-1*H*-pyrrol-1-yl)benzoate (MAP4). The synthesis procedure is the same as that of **MAP2**, and only replaced naphthalen-1-ylboronic acid by anthracen-2-ylboronic acid (0.6663 g, 3.00 mmol). The yield of **MAP4** gives 46.6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 2H), 8.23 (s, 2H), 8.00-7.90 (m, 6H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.74 (s, 2H), 7.47-7.39 (m, 4H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.72 (s, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.94, 143.04, 136.11, 131.98, 131.78, 131.41, 130.36, 130.27, 129.64, 129.18, 128.69, 128.16, 128.05, 127.78, 127.23, 126.68, 126.23, 125.94, 125.53, 125.38, 111.58, 61.21, 14.24. MS (MALDI, *m/z*) Calcd for $C_{41}H_{29}NO_2$ $[M]^+$: 567.22, found: 566.99.

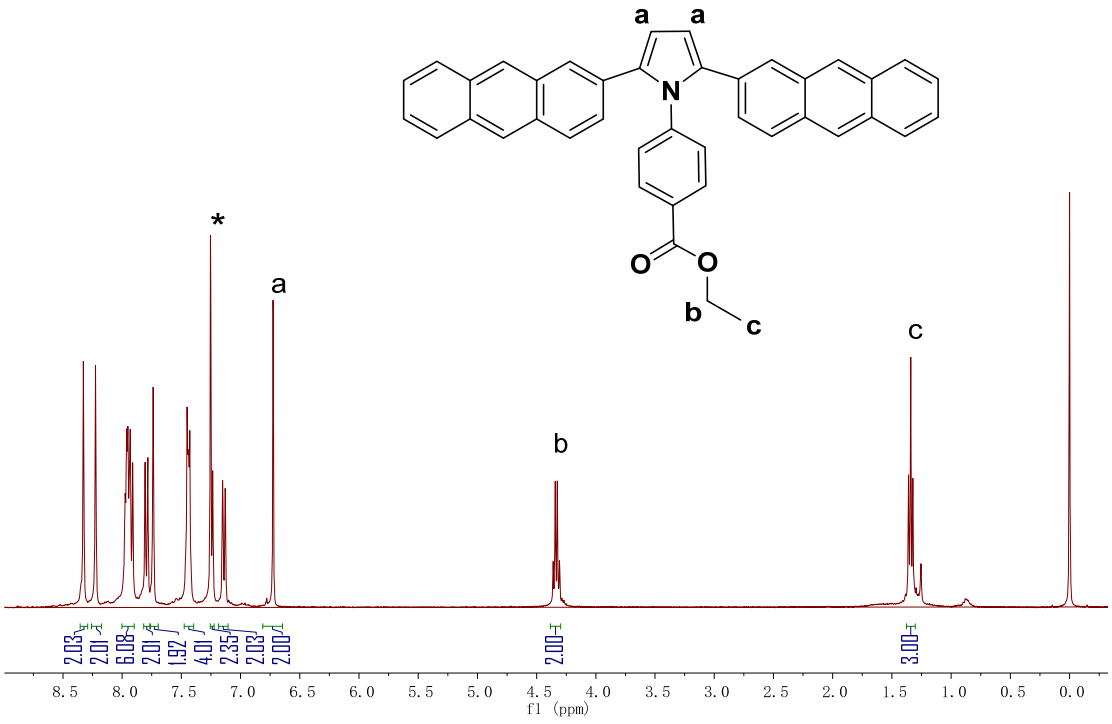


Figure S7. ^{1}H NMR spectrum of **MAP4** in $CDCl_3$.

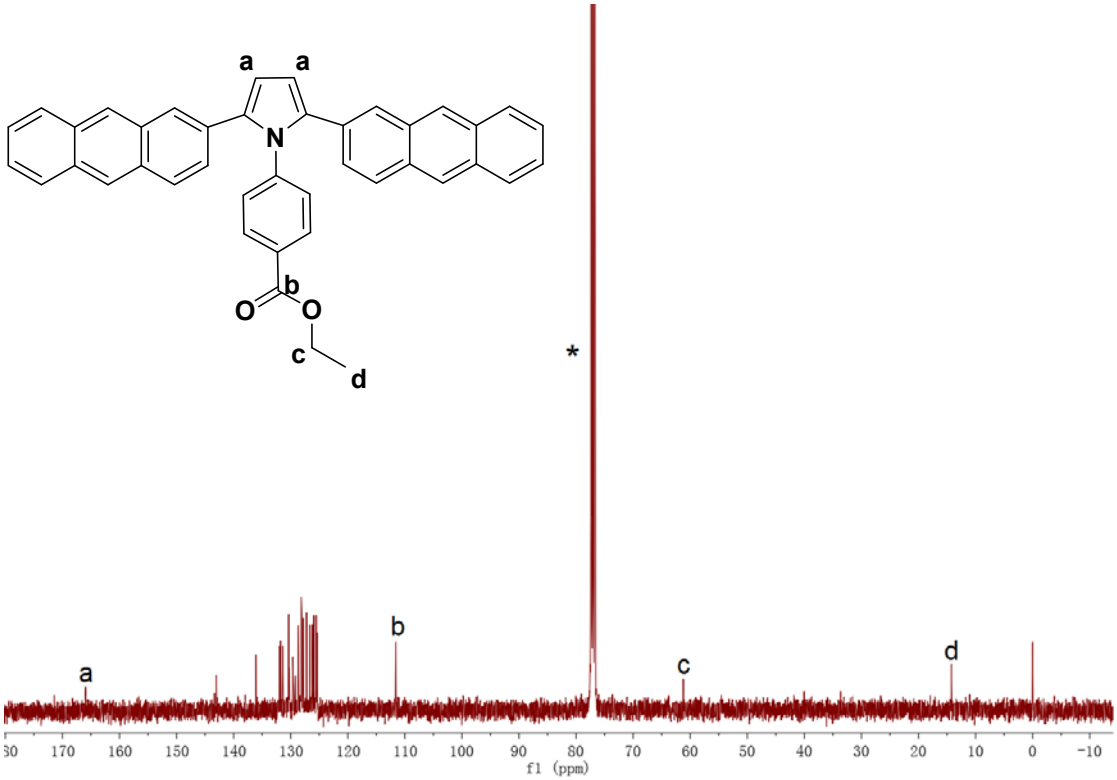


Figure S8. ^{13}C NMR spectrum of **MAP4** in $CDCl_3$.

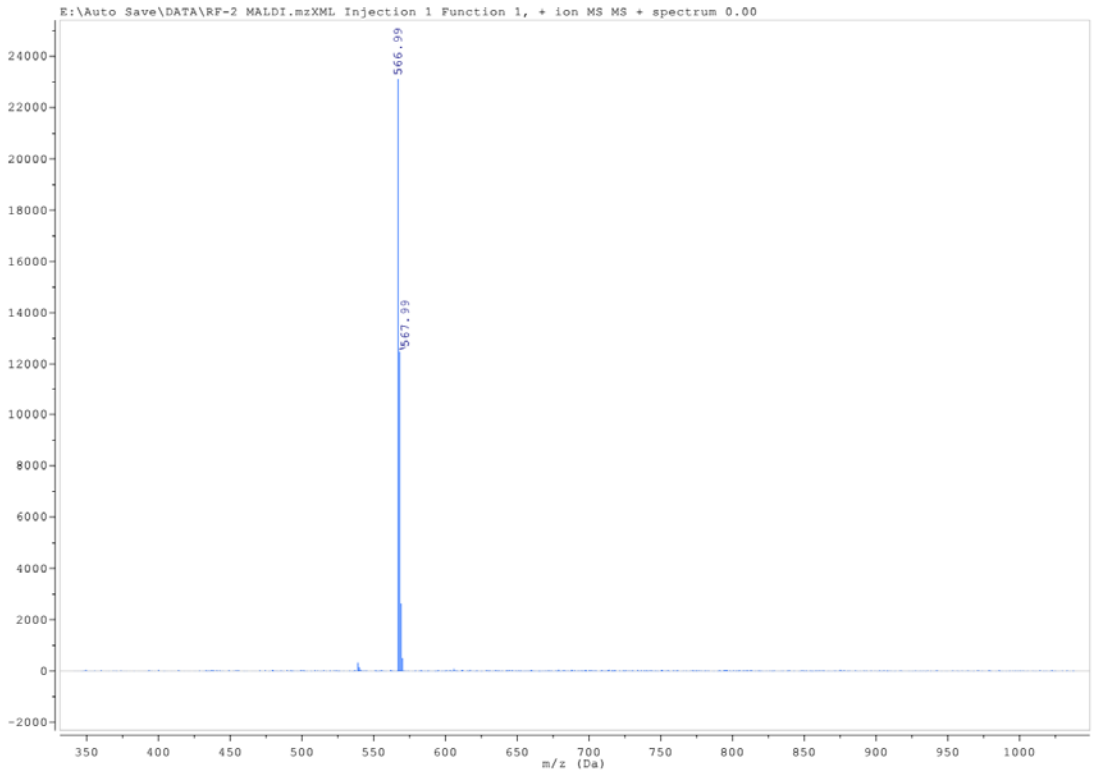


Figure S9. MS spectrum of **MAP4**.

Synthesis of ethyl 4-(2,5-di(anthracen-9-yl)-1*H*-pyrrol-1-yl)benzoate (MAP5). The synthesis procedure is the same as that of **MAP2**, and only replaced naphthalen-1-ylboronic acid by anthracen-9-ylboronic acid (0.6663 g, 3.00 mmol). The yield of **MAP5** gives 51.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 2H), 8.11 (d, *J* = 8.8 Hz, 4H), 7.94 (d, *J* = 8.4 Hz, 4H), 7.59-7.35 (m, 8H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.82 (s, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 3.94 (q, *J* = 7.2 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.59, 142.52, 132.42, 131.19, 130.21, 128.86, 128.54, 127.94, 127.80, 126.50, 126.13, 125.89, 125.18, 113.43, 60.67, 14.01. MS (MALDI, *m/z*) Calcd for $C_{41}H_{29}NO_2$ $[M]^+$: 567.22, found: 567.04.

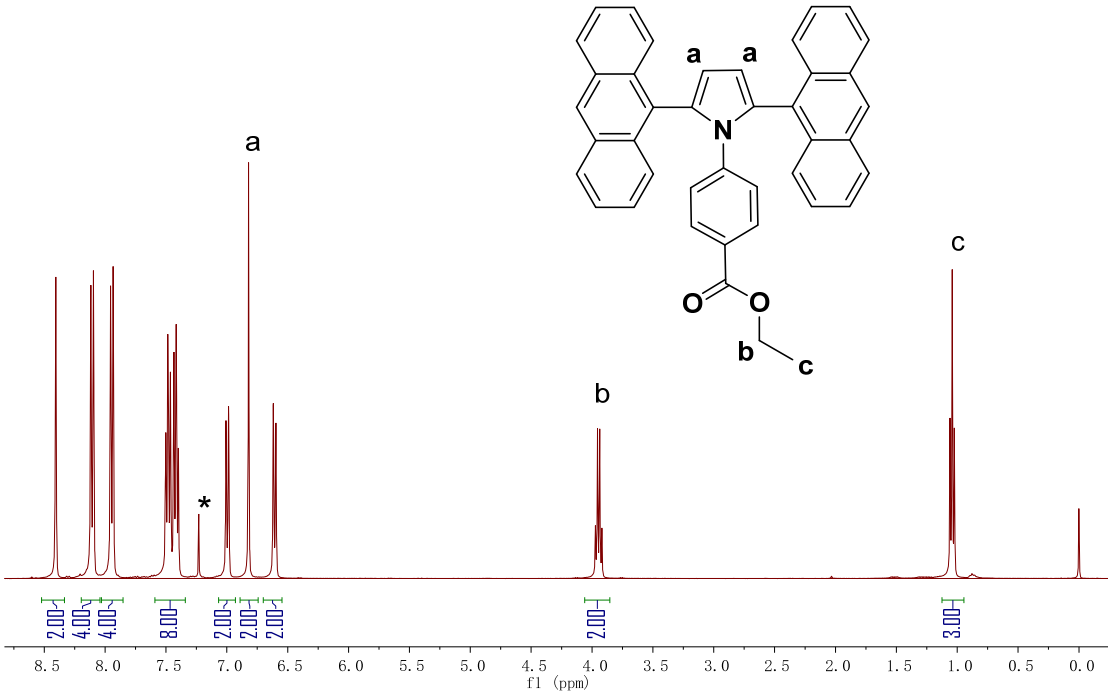


Figure S10. ^{1}H NMR spectrum of **MAP5** in $CDCl_3$.

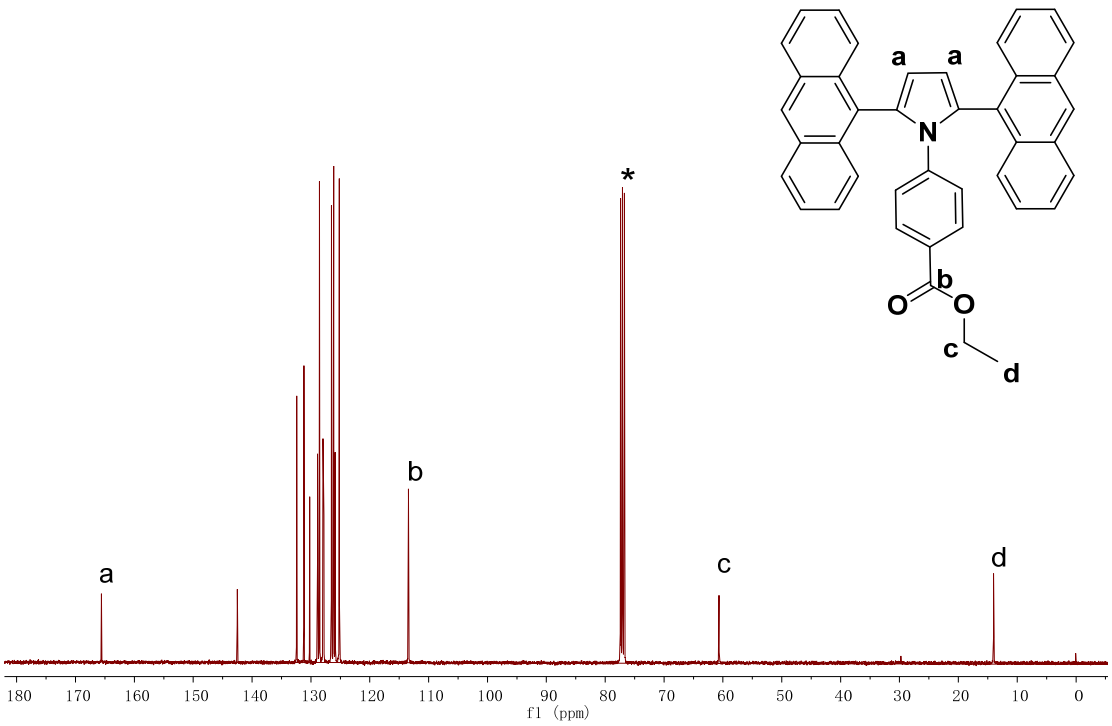


Figure S11. ^{13}C NMR spectrum of **MAP5** in $CDCl_3$.

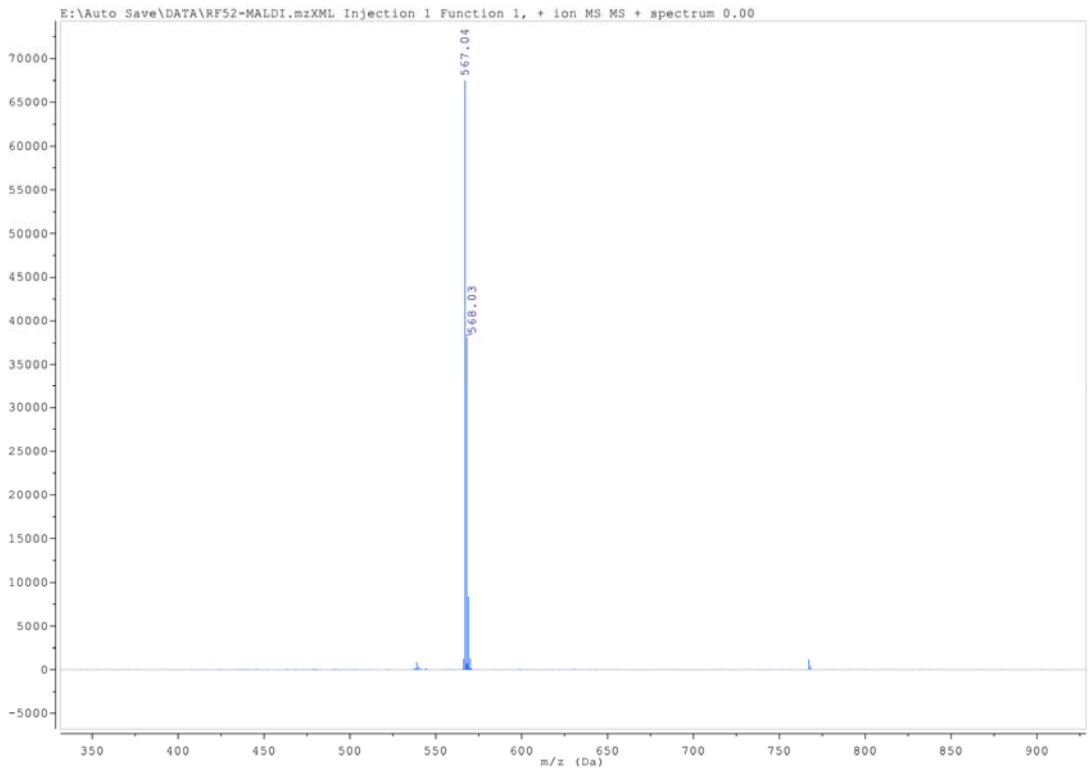


Figure S12. MS spectrum of **MAP5**.

Synthesis of ethyl 4-(2,5-di(pyren-1-yl)-1*H*-pyrrol-1-yl)benzoate (MAP6). The synthesis procedure is the same as that of **MAP2**, and only replaced naphthalen-1-ylboronic acid by pyren-1-ylboronic acid (0.7383 g, 3.00 mmol). The yield of **MAP6** gives 72.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 4.8 Hz, 2H), 8.19 (d, *J* = 2.8 Hz, 2H), 8.17 (d, *J* = 2.4 Hz, 2H), 8.07 (d, *J* = 9.2 Hz, 4H), 8.04-7.95 (m, 6H), 7.74 (d, *J* = 6.0 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 2H), 4.07 (q, *J* = 7.2 Hz, 2H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.63, 142.76, 133.25, 131.36, 130.97, 130.61, 130.39, 129.54, 129.13, 128.31, 128.00, 127.71, 127.66, 127.54, 127.33, 126.06, 125.49, 125.23, 125.05, 124.86, 124.71, 124.17, 113.25, 60.81, 14.04. MS (MALDI, *m/z*) Calcd for $C_{45}H_{29}NO_2$ $[M]^+$: 615.22, found: 615.04.

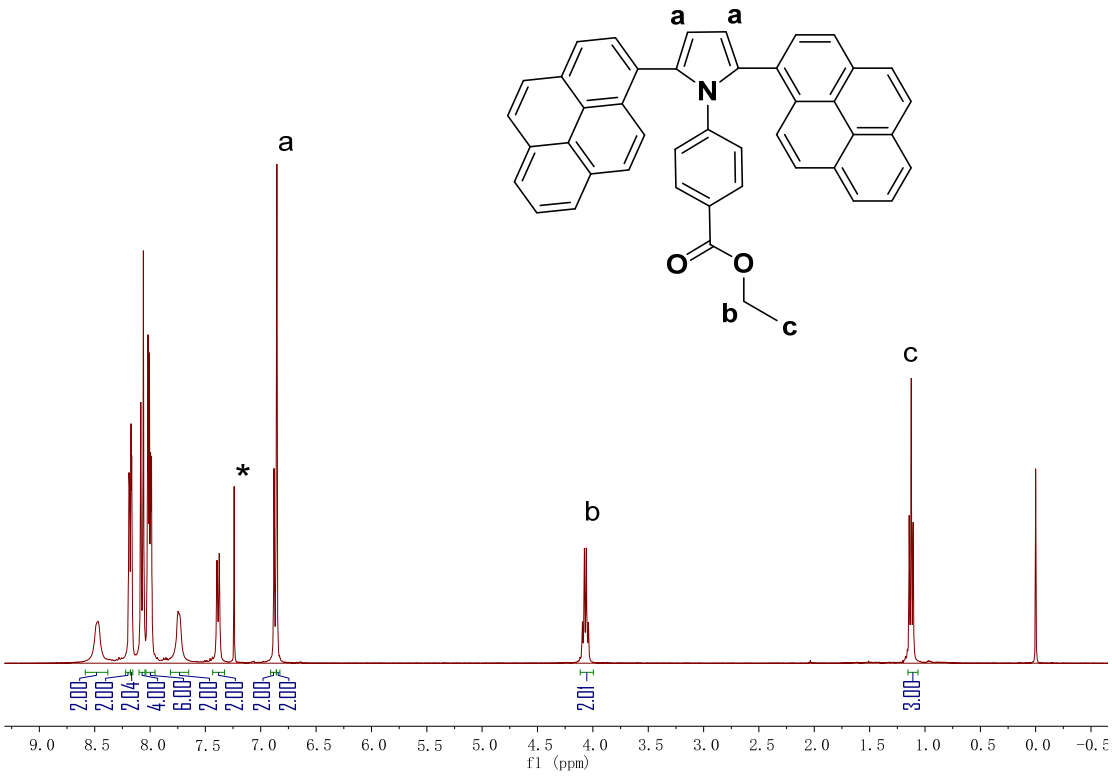


Figure S13. ^{1}H NMR spectrum of **MAP6** in $CDCl_3$.

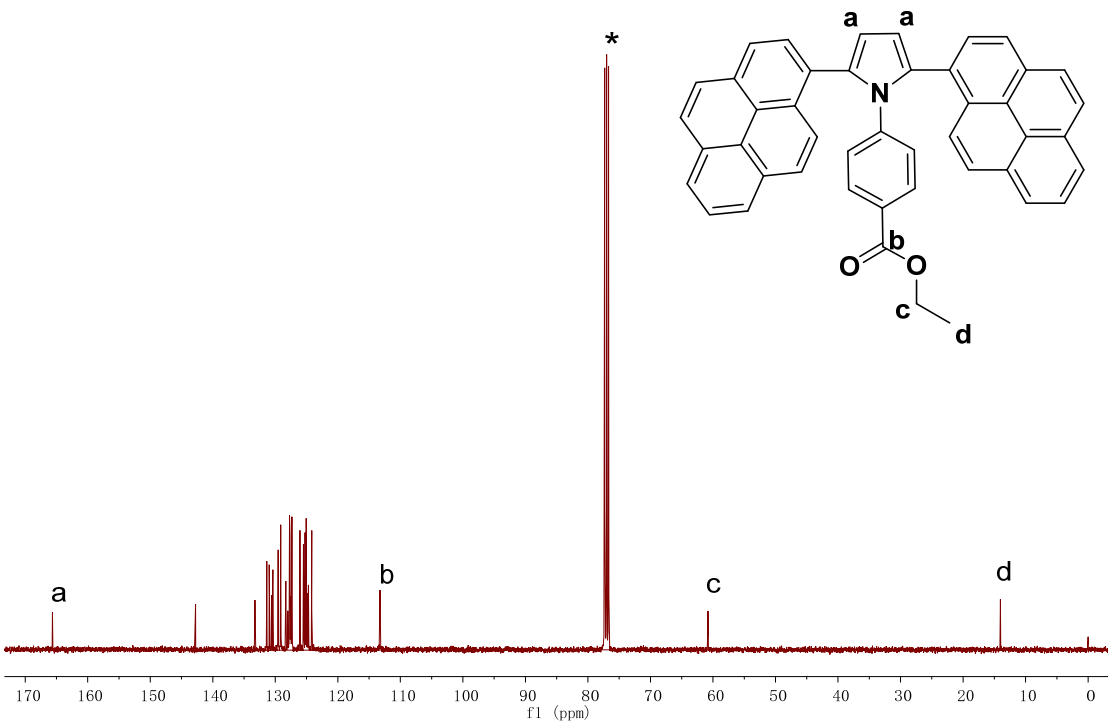


Figure S14. ^{13}C NMR spectrum of **MAP6** in $CDCl_3$.

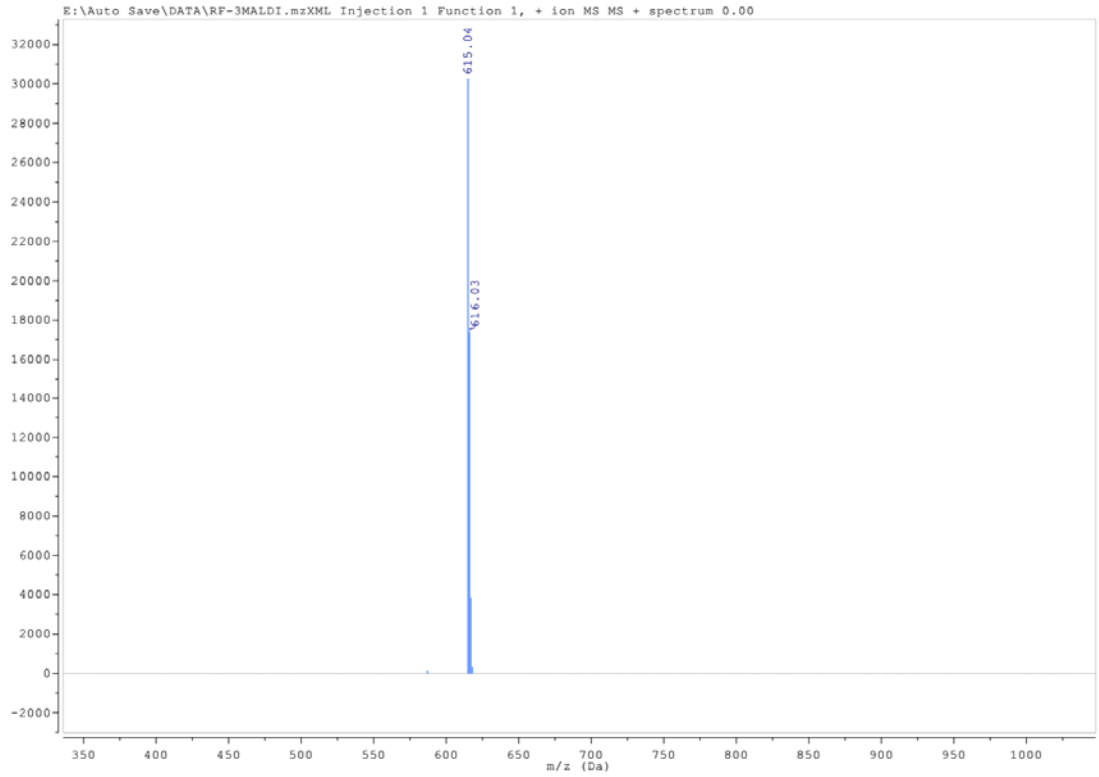


Figure S15. MS spectrum of **MAP6**.

The general synthesis procedure for MAP-CHO. $POCl_3$ (100 μL, 1.10 mmol) was dropped slowly into DMF (15 mL) at 0 °C and stirred for 1 h at room temperature. A dichloromethane solution of **MAP2** (0.4672 g, 1.00 mmol) was added to the above solution. After the mixture stirred for 12 h at room temperature, the residue was poured into a dilute aqueous solution of NaOH (150 mL) and extracted with dichloromethane. Then, the solution of dichloromethane was dried over anhydrous $MgSO_4$ and filtered by suction. The solvent was evaporated by vacuum distillation. The crude product was purified by gel chromatography using a dichloromethane/petroleum ether mixture (1/2, V_d/V_p) as the eluent. **MAP-CHO** was obtained with a certain yield.

MAP2-CHO: The yield gives 46.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.54 (s, 1H), 8.08-8.00 (m, 1H), 7.89-7.72 (m, 5H), 7.52-7.39 (m, 8H), 7.36-7.26 (m, 2H), 7.14 (s, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.83, 165.41, 141.96, 141.14, 134.52, 133.51, 133.28, 132.66, 130.56, 129.91, 129.52, 129.42, 129.21, 129.11, 128.88, 128.42, 128.34, 127.13, 126.94, 126.64, 126.36, 126.11, 125.71, 125.60, 125.42, 124.86, 124.78, 109.78, 61.09, 14.10. HR-MS (EI, *m/z*) Calcd for $C_{34}H_{25}NO_3$ $[M]^+$: 495.1829, found: 495.1831, error 0.40 ppm.

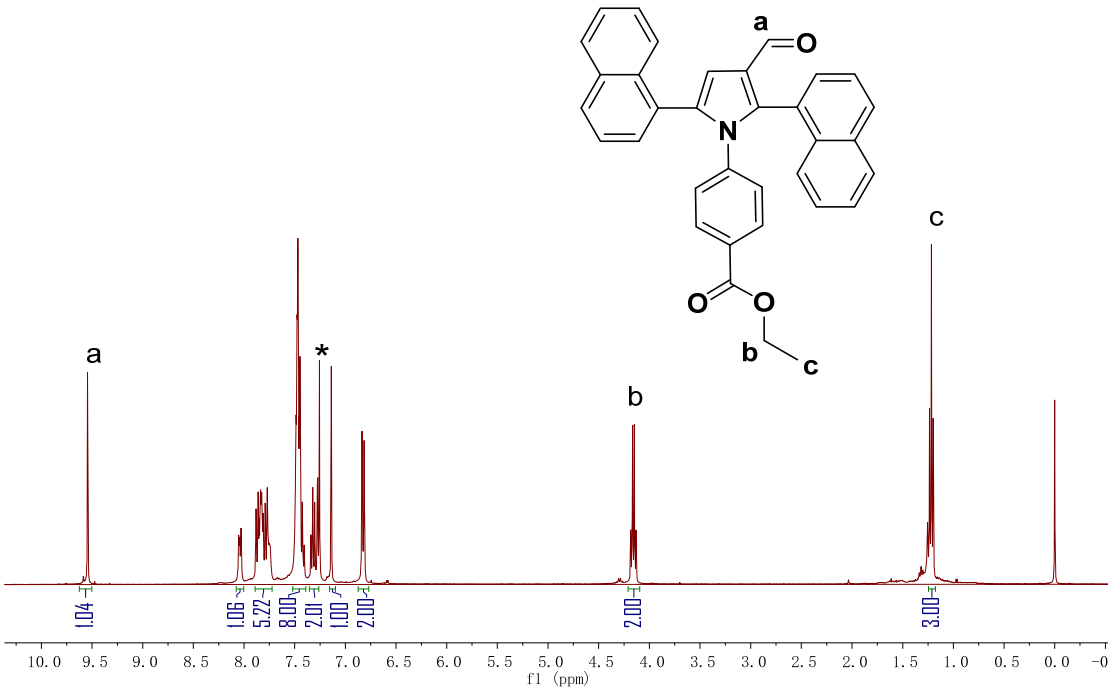


Figure S16. ^{1}H NMR spectrum of **MAP2-CHO** in $CDCl_3$.

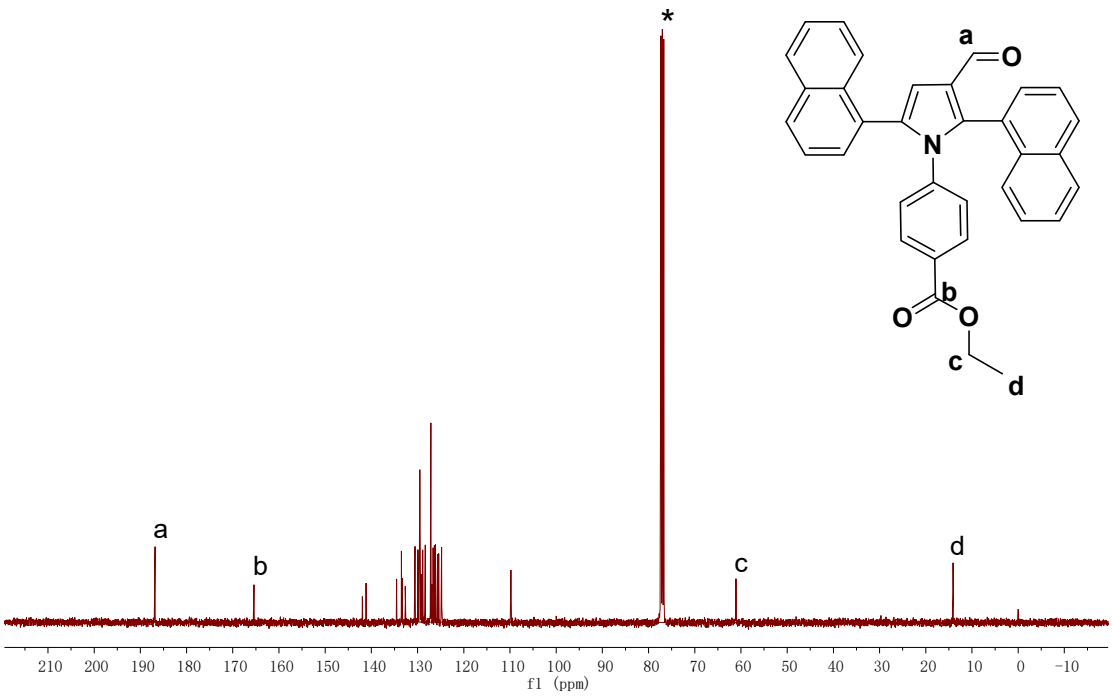


Figure S17. ^{13}C NMR spectrum of **MAP2-CHO** in $CDCl_3$.

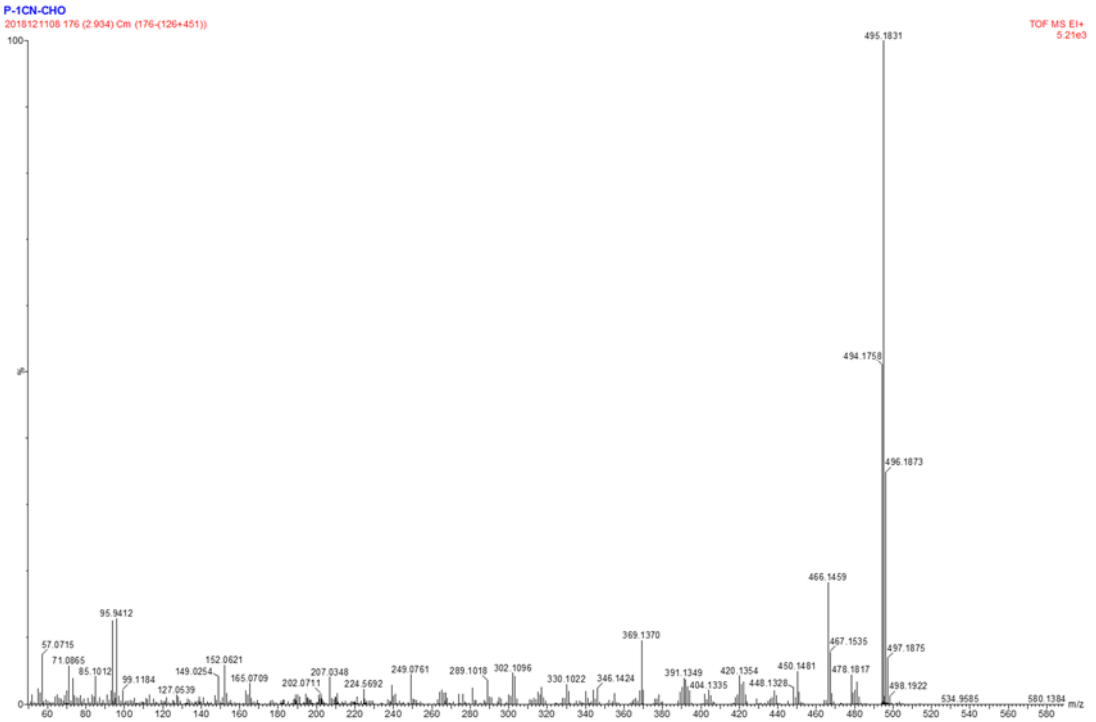


Figure S18. HR-MS spectrum of **MAP2-CHO**.

MAP3-CHO: The yield gives 57.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.80 (s, 1H), 7.87-7.74 (m, 6H), 7.71-7.62 (m, 4H), 7.56-7.50 (m, 2H), 7.48-7.40 (m, 2H), 7.16-7.07 (m, 5H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 187.04, 165.51, 144.05, 141.25, 136.73, 133.07, 132.86, 132.66, 132.39, 131.23, 130.33, 129.88, 128.79, 128.57, 128.21, 128.08, 127.94, 127.86, 127.75, 127.61, 127.16, 126.85, 126.48, 126.43, 124.93, 108.57, 61.32, 14.20. HR-MS (EI, *m/z*) Calcd for $C_{34}H_{25}NO_3$ $[M]^+$: 495.1829, found: 495.1819, error -2.02 ppm.

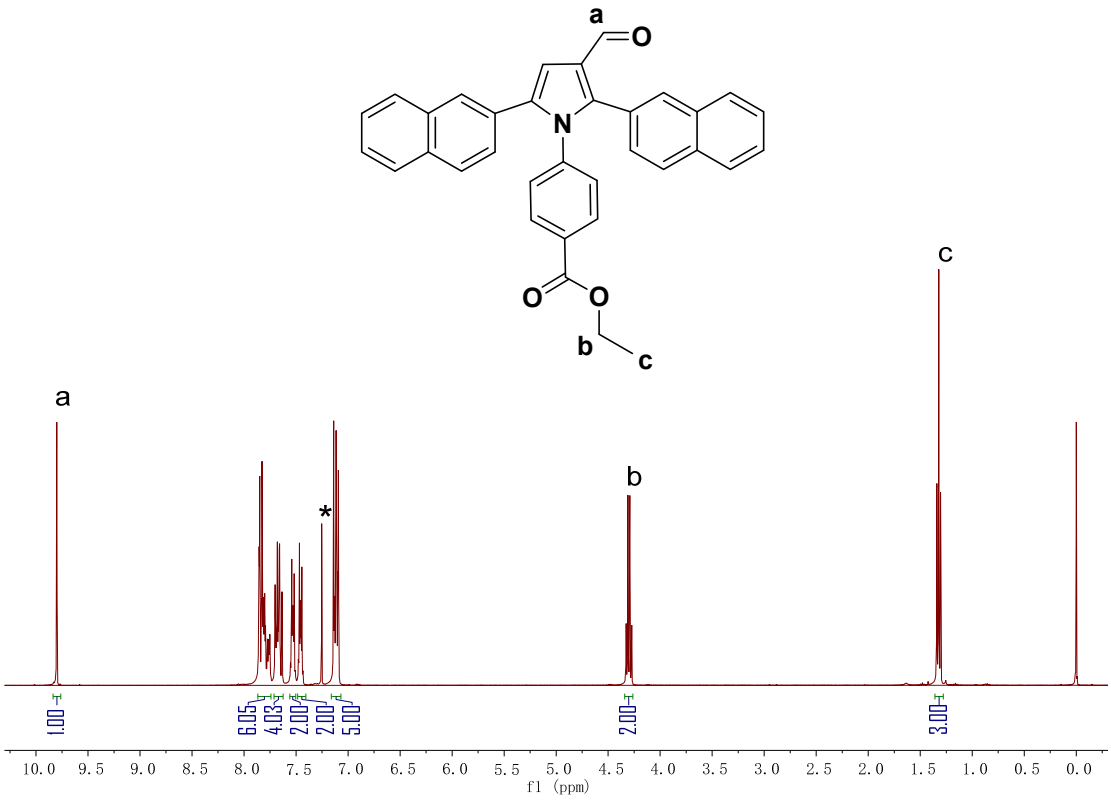


Figure S19. ^{1}H NMR spectrum of **MAP3-CHO** in $CDCl_3$.

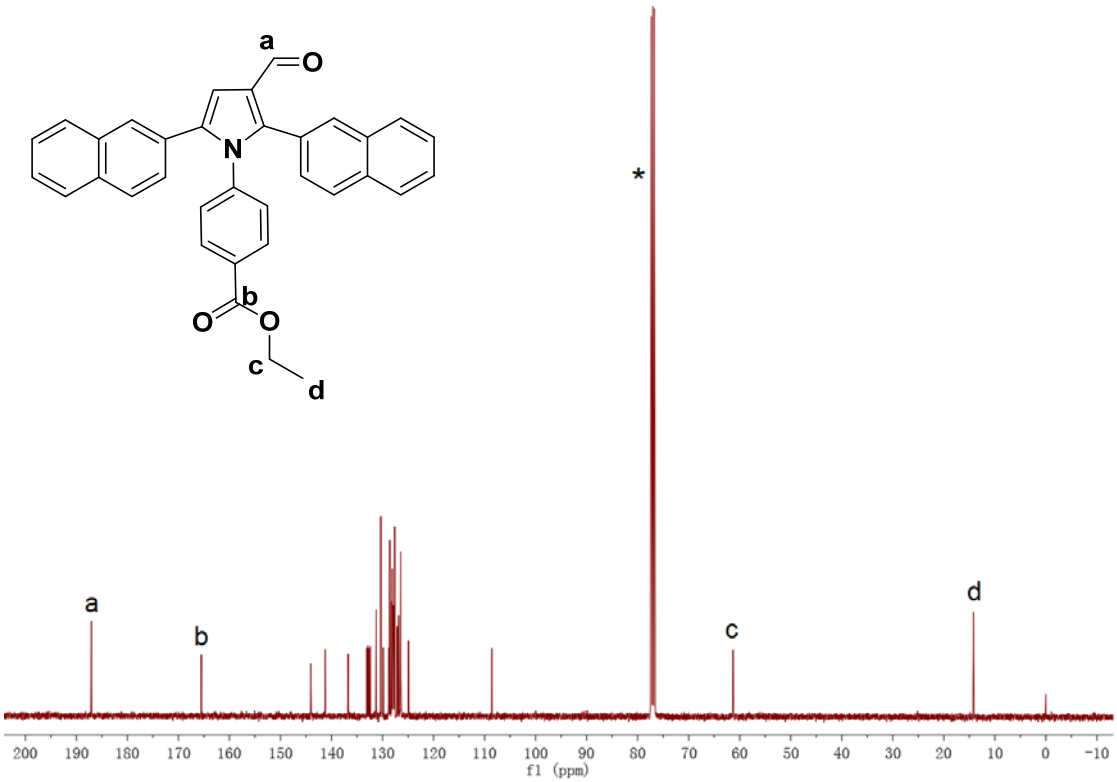


Figure S20. ^{13}C NMR spectrum of **MAP3-CHO** in $CDCl_3$.

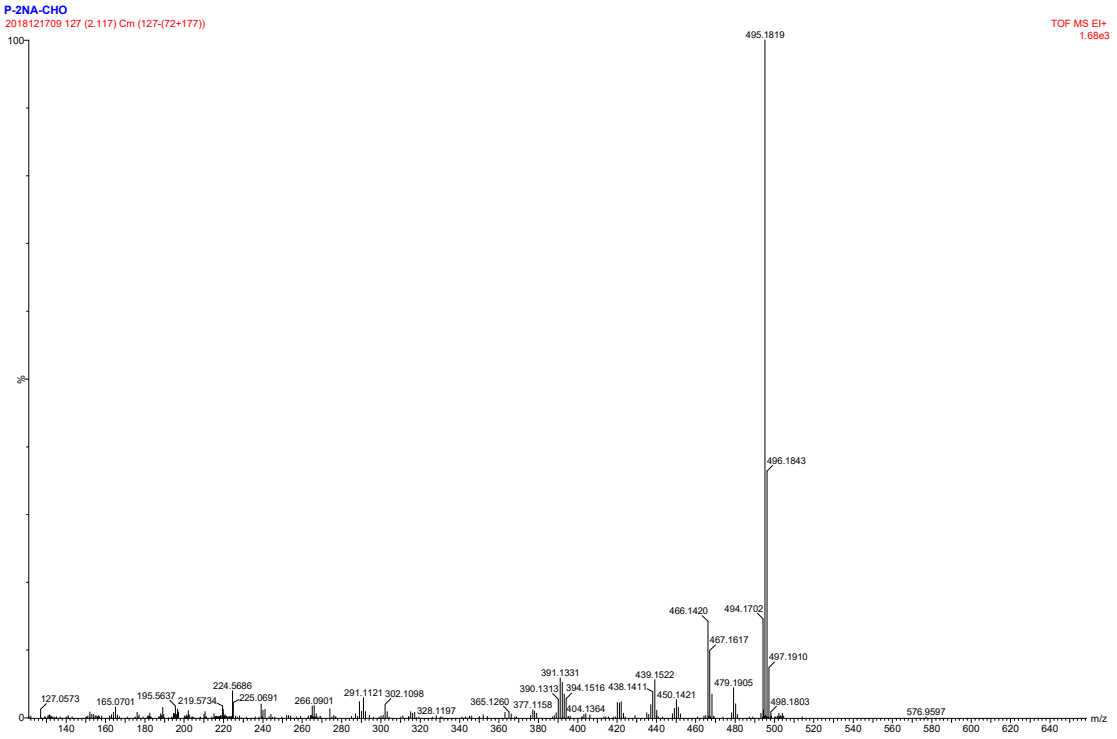


Figure S21. HR-MS spectrum of **MAP3-CHO**.

MAP4-CHO: The yield gives 55.7%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.88 (s, 1H), 8.40 (d, *J* = 8.0 Hz, 2H), 8.34 (s, 1H), 8.25 (s, 1H), 8.09-7.93 (m, 5H), 7.90-7.75 (m, 5H), 7.57-7.49 (m, 2H), 7.48-7.37 (m, 2H), 7.24-7.15 (m, 3H),7.15-7.10 (m, 1H), 7.09-7.03 (m, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 187.03, 165.52, 144.19, 141.37, 136.82, 132.44, 132.18, 132.05, 131.71, 131.12, 130.60, 130.42, 129.97, 128.51, 128.26, 128.22, 128.16, 128.11, 126.99, 126.72, 126.57, 126.29, 126.12, 126.07, 126.00, 125.84, 125.74, 125.05, 108.81, 61.33, 14.18. HR-MS (APCI, *m/z*) Calcd for $C_{42}H_{29}NO_3$ $[M+H]^+$: 596.2220, found: 596.2223, error 0.45 ppm.

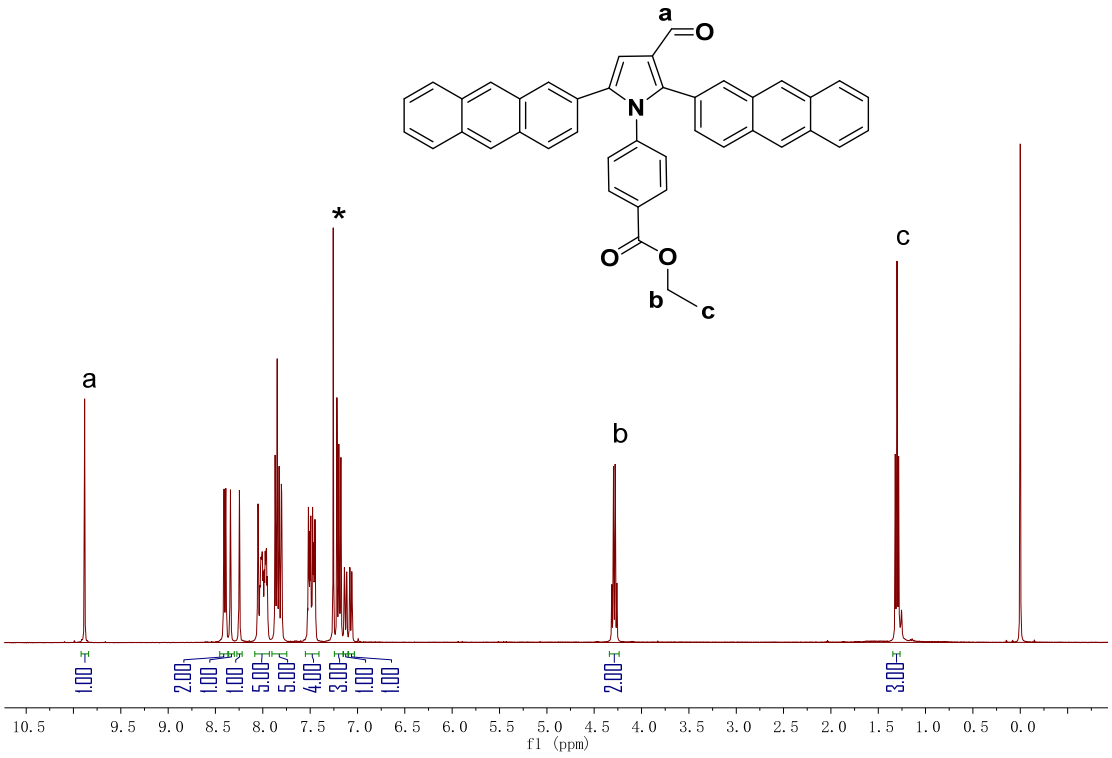


Figure S22. ^{1}H NMR spectrum of **MAP4-CHO** in $CDCl_3$.

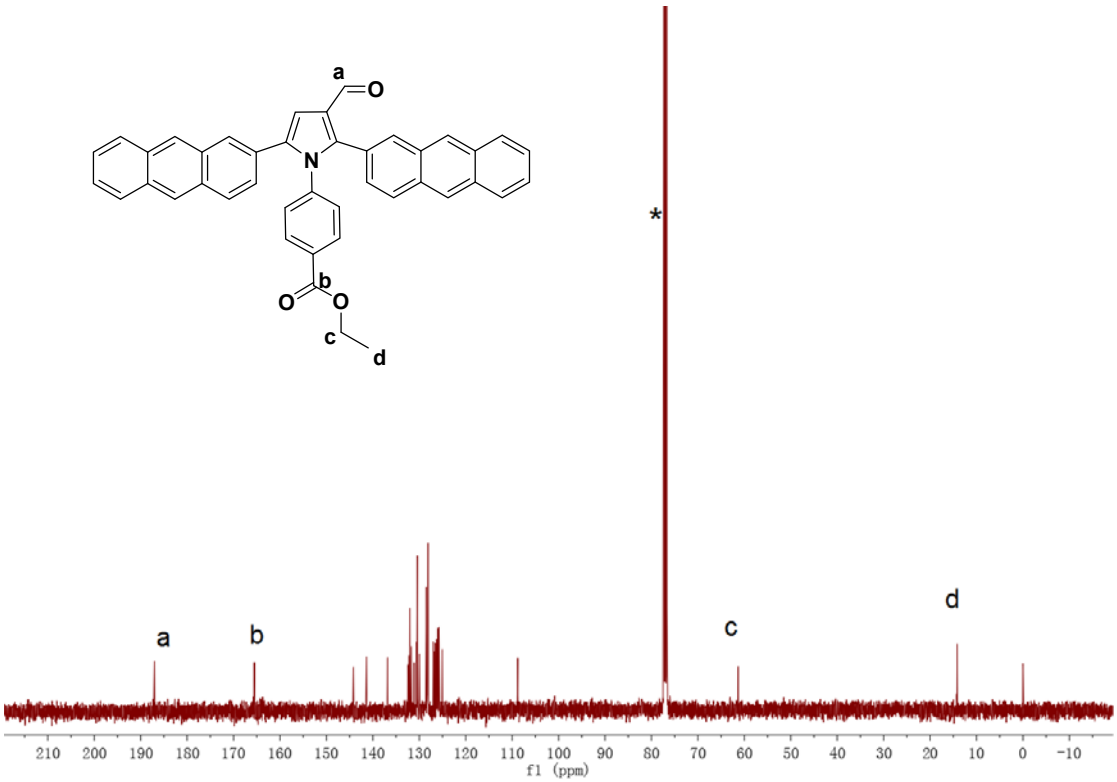


Figure S23. ^{13}C NMR spectrum of **MAP4-CHO** in $CDCl_3$.

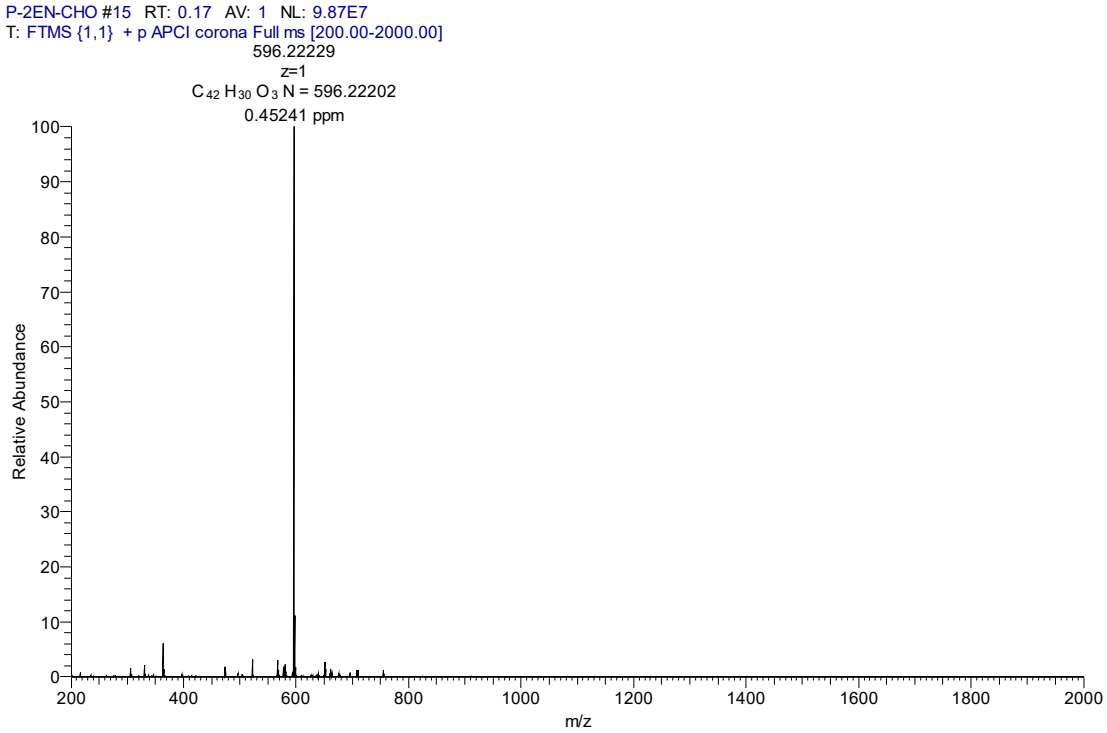


Figure S24. HR-MS spectrum of **MAP4-CHO**.

MAP5-CHO: The yield gives 54.2%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (s, 1H), 8.51 (s, 1H), 8.44 (s, 1H), 8.06 (d, *J* = 9.2 Hz, 2H), 8.02-7.91 (m, 6H), 7.59-7.51 (m, 4H), 7.50-7.42 (m, 4H), 7.34 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.82, 165.18, 140.62, 140.48, 132.89, 132.80, 132.12, 131.04, 130.91, 129.61, 129.14, 128.96, 128.88, 128.83, 128.71, 127.28, 126.80, 126.66, 125.97, 125.83, 125.49, 125.41, 125.33, 122.83, 111.10, 60.89, 13.97. HR-MS (EI, *m/z*) Calcd for $C_{42}H_{29}NO_3$ $[M]^+$: 595.2142, found: 595.2135, error -1.18 ppm.

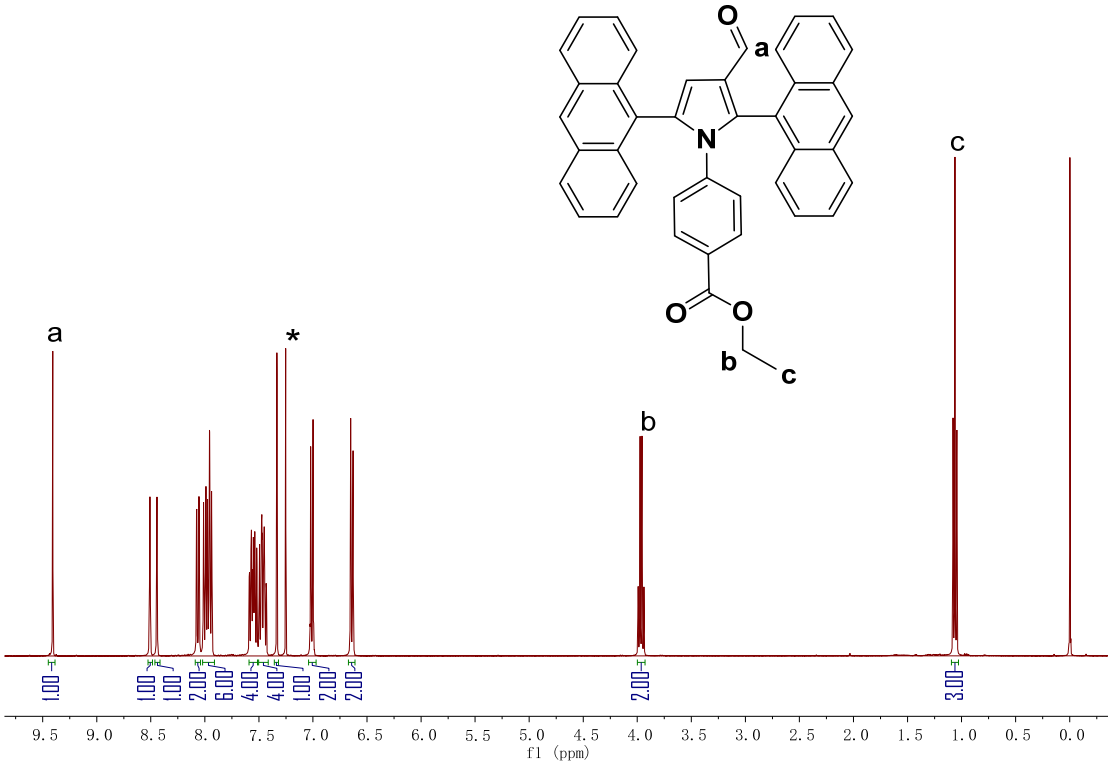


Figure S25. ^{1}H NMR spectrum of **MAP5-CHO** in $CDCl_3$.

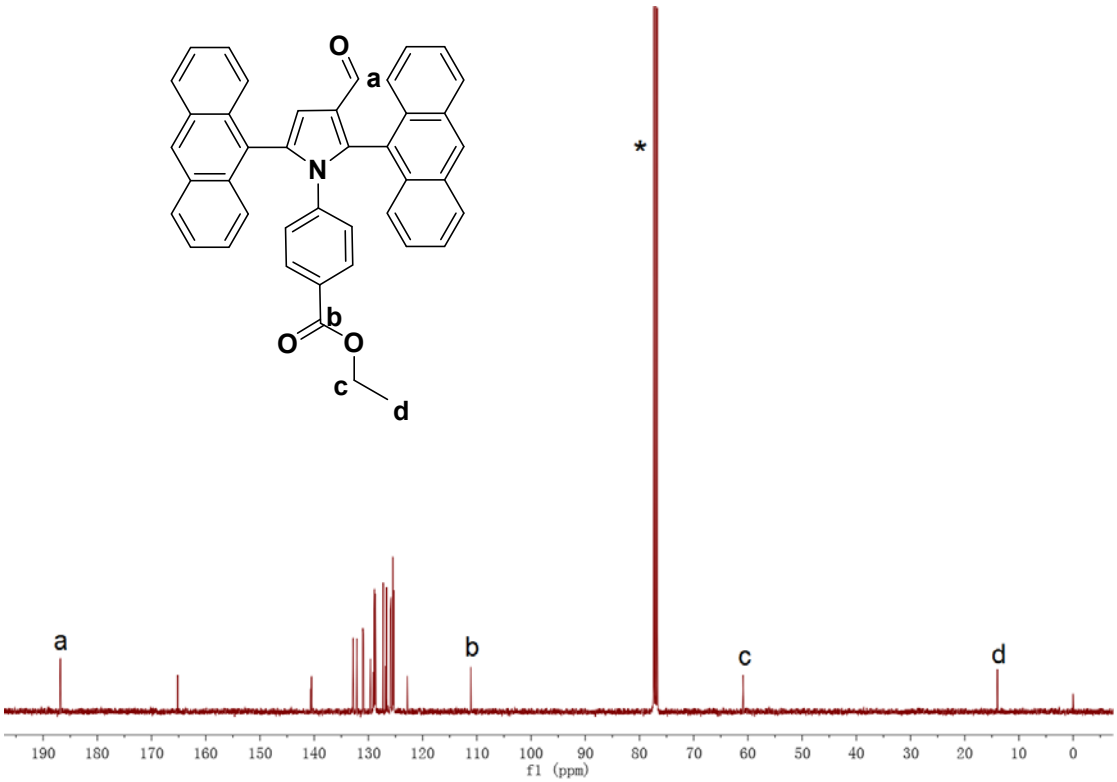


Figure S26. ^{13}C NMR spectrum of **MAP5-CHO** in $CDCl_3$.

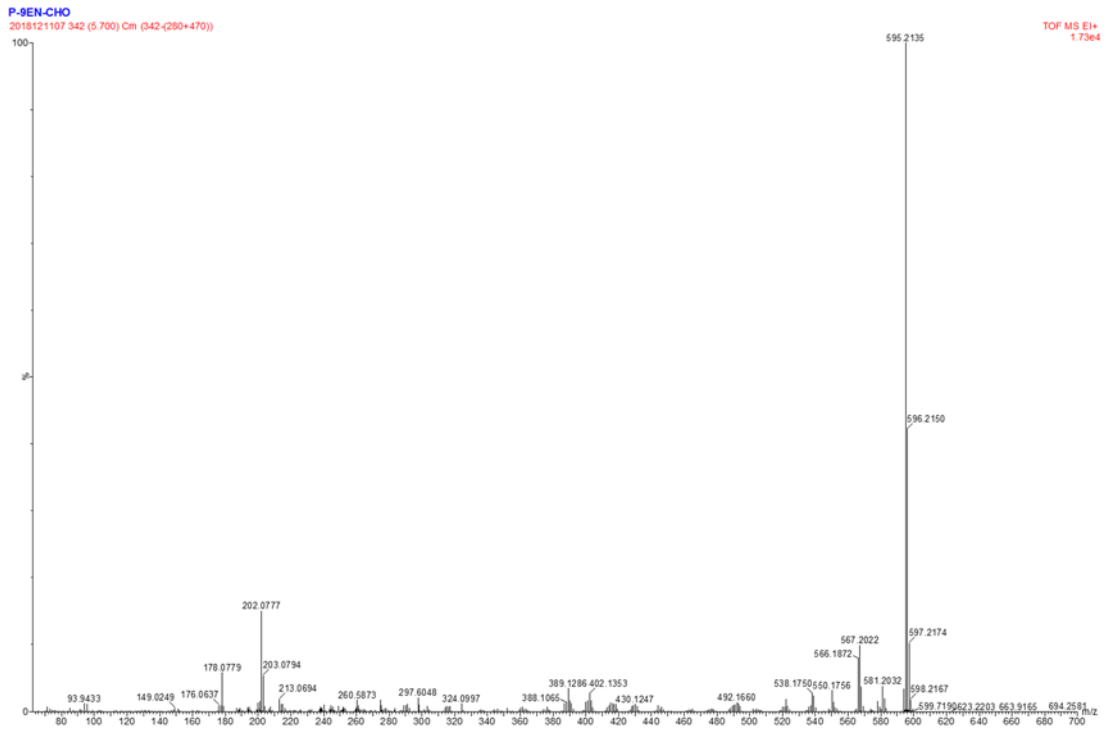


Figure S27. HR-MS spectrum of **MAP5-CHO**.

MAP6-CHO: The yield gives 60.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.62 (s, 1H), 8.41 (d, *J* = 9.2 Hz, 1H), 8.26-8.20 (m, 4H),8.16-8.10 (m, 5H), 8.10-8.04 (m, 3H), 8.04-7.92 (m, 4H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.38-7.30 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 187.04, 165.18, 141.12, 135.10, 131.98, 131.61, 131.28, 131.23, 130.86, 130.72, 130.47, 129.64, 129.54, 129.19, 128.96, 128.90, 128.64, 128.31, 128.15, 127.42, 127.24, 127.22, 126.46, 126.25, 126.17, 126.00, 125.81, 125.60, 125.44, 124.82, 124.76, 124.54, 124.43, 124.34, 124.21, 123.77, 110.54, 60.96, 13.98. HR-MS (EI, *m/z*) Calcd for $C_{46}H_{29}NO_3$ $[M]^+$: 643.2147, found: 643.2140, error -1.09 ppm.

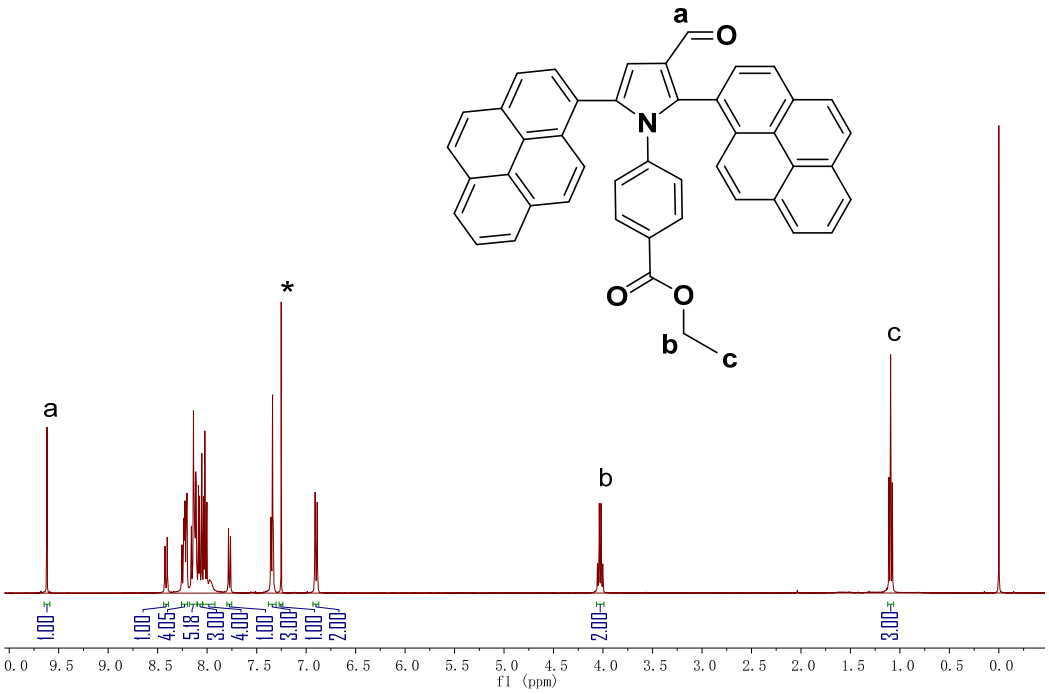


Figure S28. ^{1}H NMR spectrum of **MAP6-CHO** in $CDCl_3$.

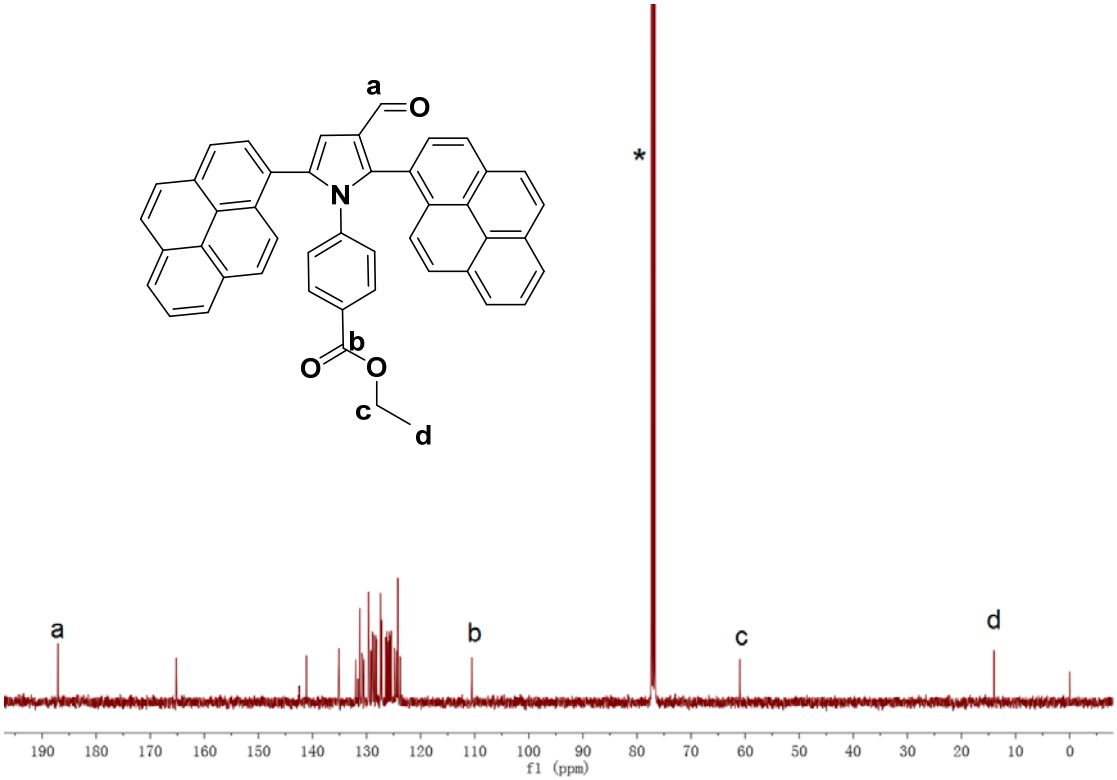


Figure S29. ^{13}C NMR spectrum of **MAP6-CHO** in $CDCl_3$.

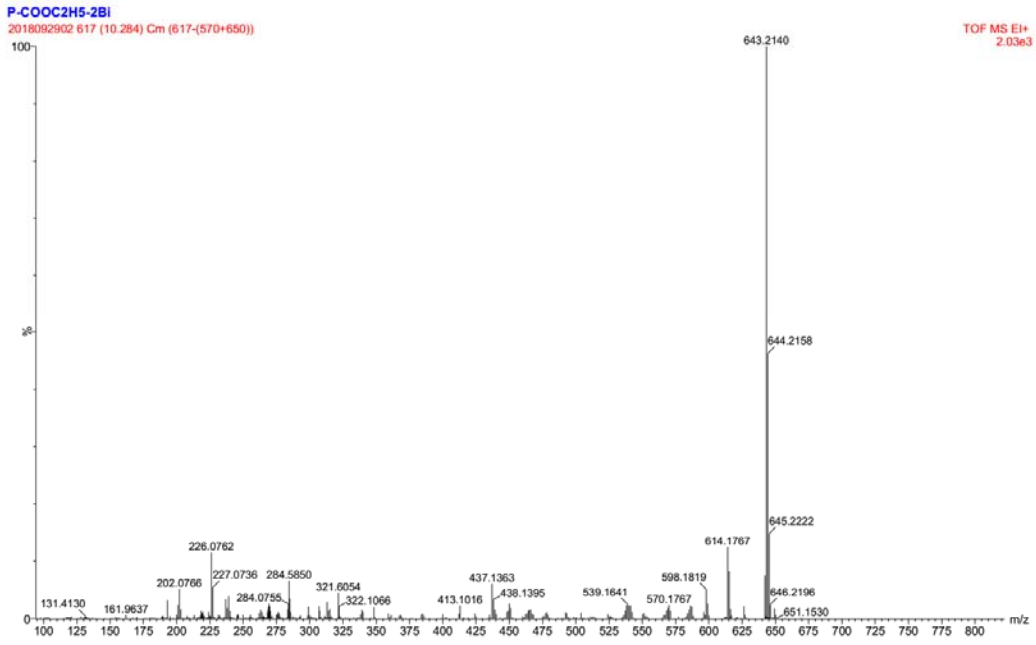


Figure S30. HR-MS spectrum of **MAP6-CHO**.

The general synthesis procedure for MAP-FE. MAP-CHO (0.50 mmol), 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (0.1905 g, 0.55 mmol) and

CH_3COONH_4 (0.0425 g, 0.55 mmol) were dissolved in 10 ml of a THF/C_2H_5OH (4/1) solvents mixture and then stirred at room temperature for 24 h. The solvent was evaporated by vacuum distillation. The crude product was purified by gel chromatography using a dichloromethane/petroleum ether mixture (3/1, Vd/Vp) as the eluent. MAP-FE was obtained with a certain yield.

MAP1-FE: The yield gives 71.3%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 7.93 (d, *J* = 16.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 1H), 7.40-7.24 (m, 8H), 7.23-7.12 (m, 4H), 7.03 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 1.65 (s, 6H) 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ = 178.21, 177.75, 176.56, 165.29, 143.15, 142.90, 141.66, 138.29, 131.34, 131.13, 130.30, 130.03, 129.63, 129.30, 129.17, 129.00, 128.95, 128.83, 128.27, 121.98, 113.63, 112.69, 112.42, 112.30, 111.97, 110.45, 108.61, 104.13, 101.81, 99.05, 93.39, 61.56, 52.79, 25.38, 23.71, 14.70, 14.52. HR-MS (APCI, *m/z*) Calcd for $C_{37}H_{28}N_4O_3$ $[M+H]^+$: 577.2234, found: 577.2230, error -0.79 ppm.

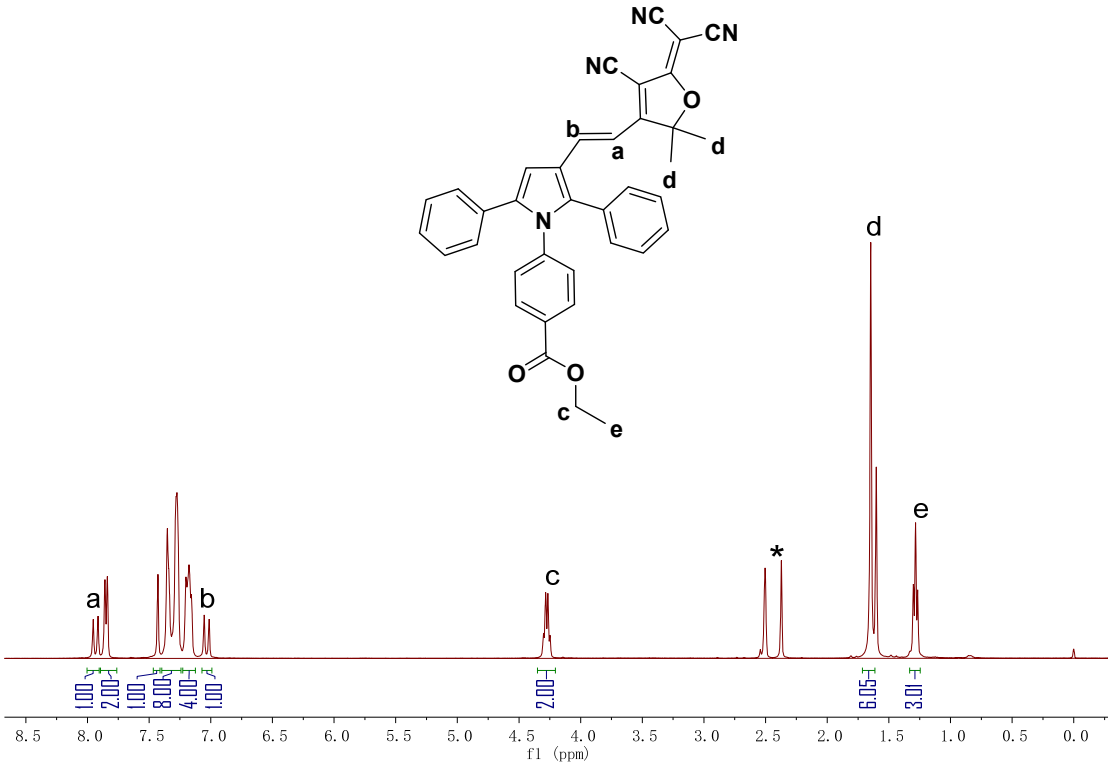


Figure S31. ^{1}H NMR spectrum of **MAP1-FE** in DMSO-*d*$_6$.

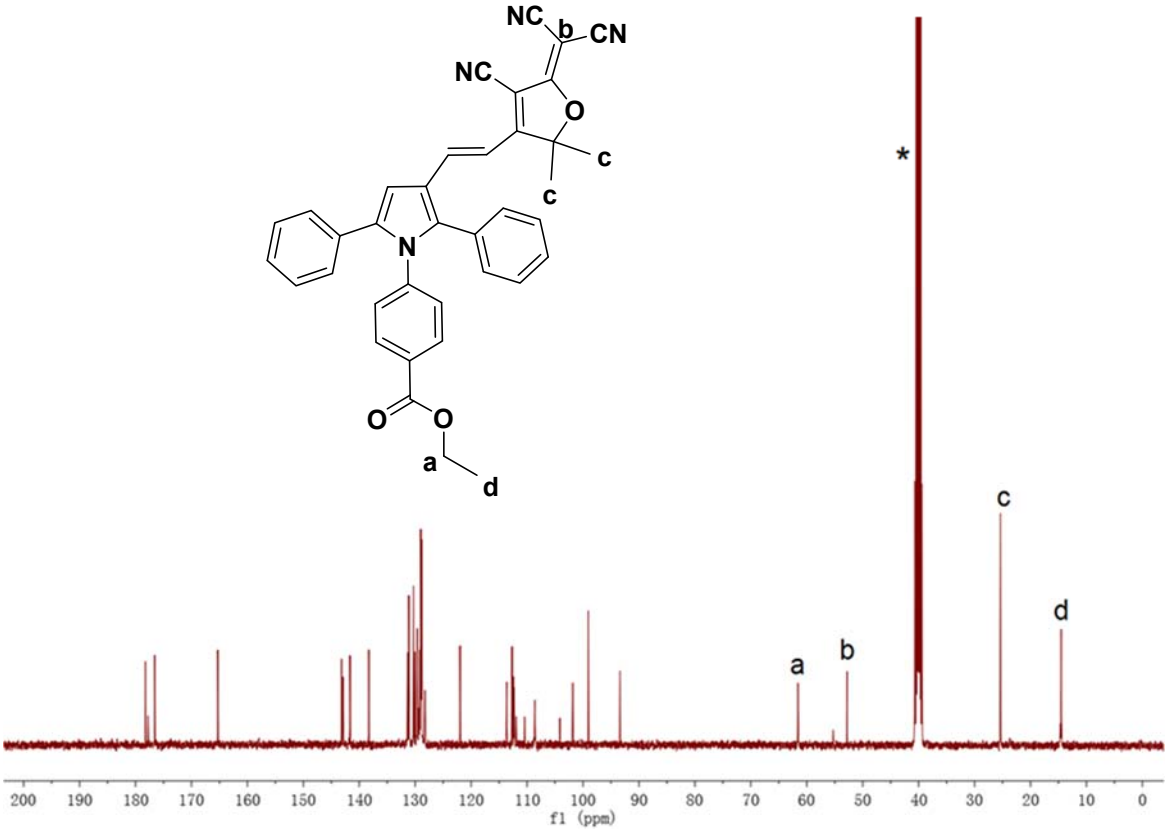


Figure S32. ^{13}C NMR spectrum of **MAP1-FE** in DMSO-*d*$_6$.

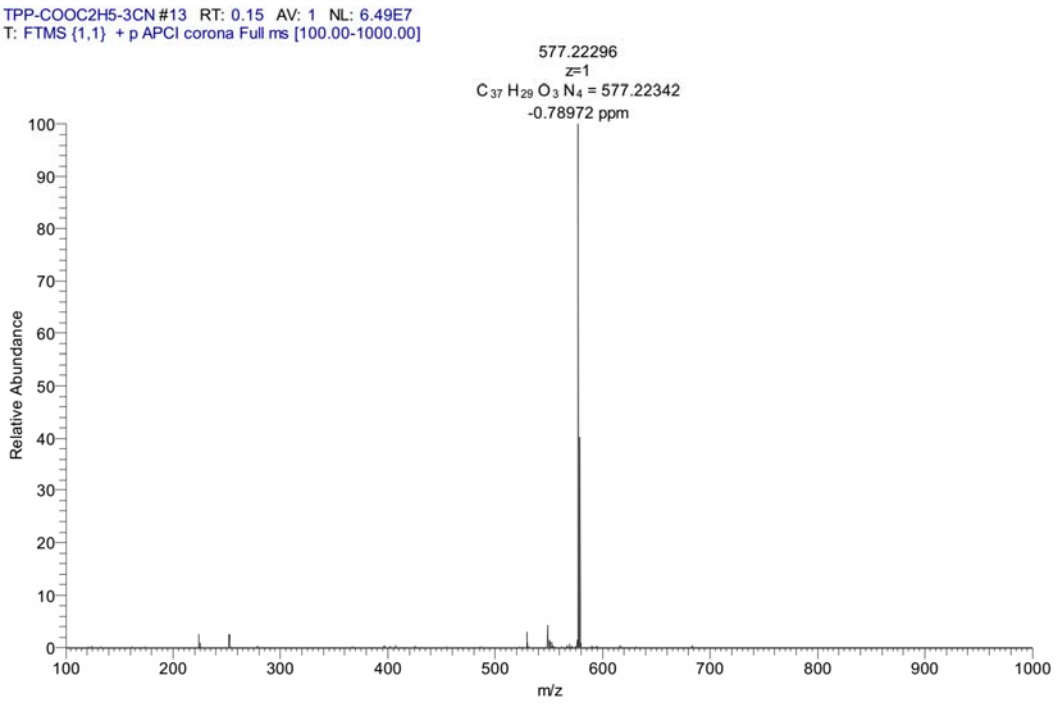


Figure S33. HR-MS spectrum of **MAP1-FE**.

MAP2-FE: The yield gives 63.5%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 7.99 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 3H), 7.76-7.67 (m, 2H), 767-7.45 (m, 9H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 1.54 (s, 3H), 1.49 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ = 177.57, 175.60, 164.39, 142.03, 141.03, 140.32, 135.62, 132.84, 132.78, 132.09, 131.89, 130.65, 129.80, 129.48, 128.89, 128.72, 128.53, 128.23, 128.09, 127.57, 127.03, 126.68, 126.28, 126.17, 126.07, 125.43, 125.06, 124.99, 124.94, 122.55, 113.02, 112.03, 111.55, 111.46, 110.04, 98.38, 92.89, 60.74, 52.13, 24.70, 24.66, 23.12, 13.77. HR-MS (ESI, *m/z*) Calcd for $C_{45}H_{32}N_4O_3$ [M-H]$^-$: 675.2402, found: 675.2387, error -2.25 ppm.

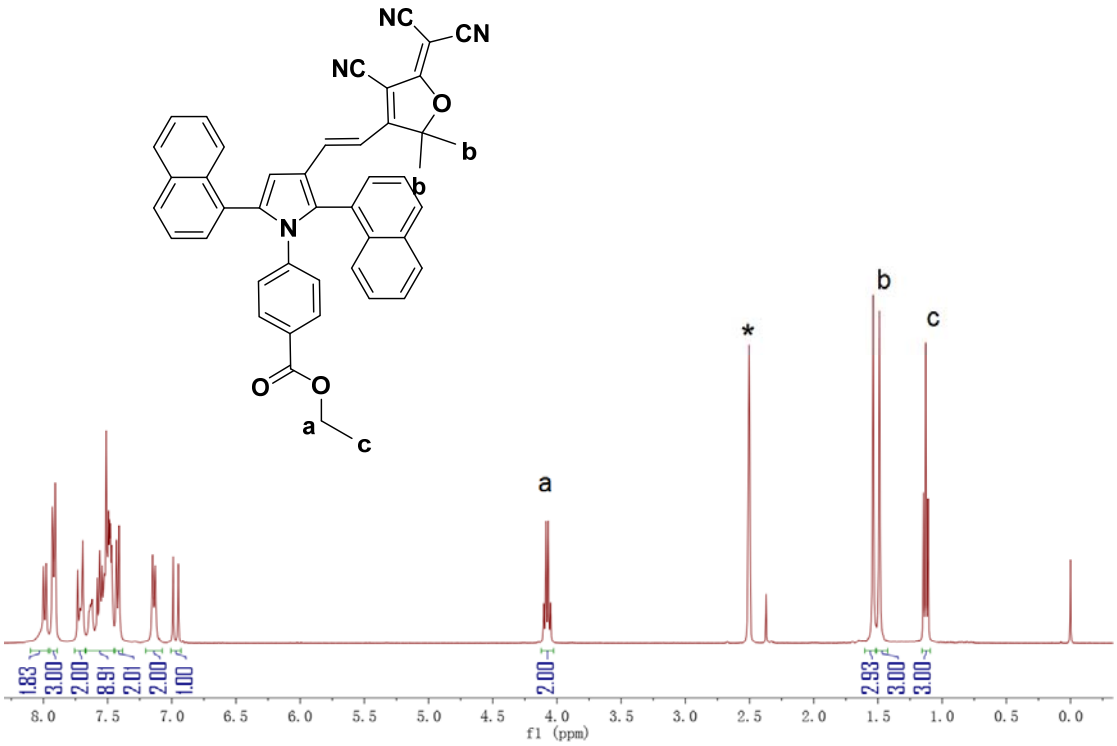


Figure S34. ^{1}H NMR spectrum of **MAP2-FE** in DMSO-*d*$_6$.

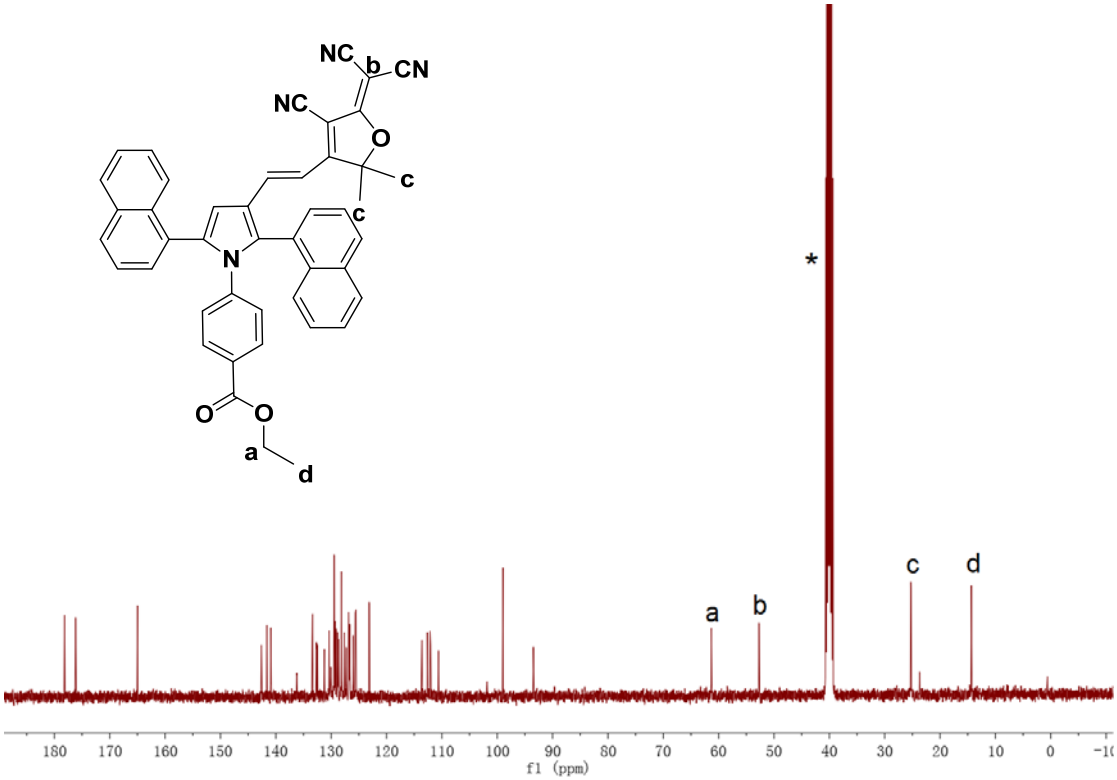


Figure S35. ^{13}C NMR spectrum of **MAP2-FE** in DMSO-d_6.

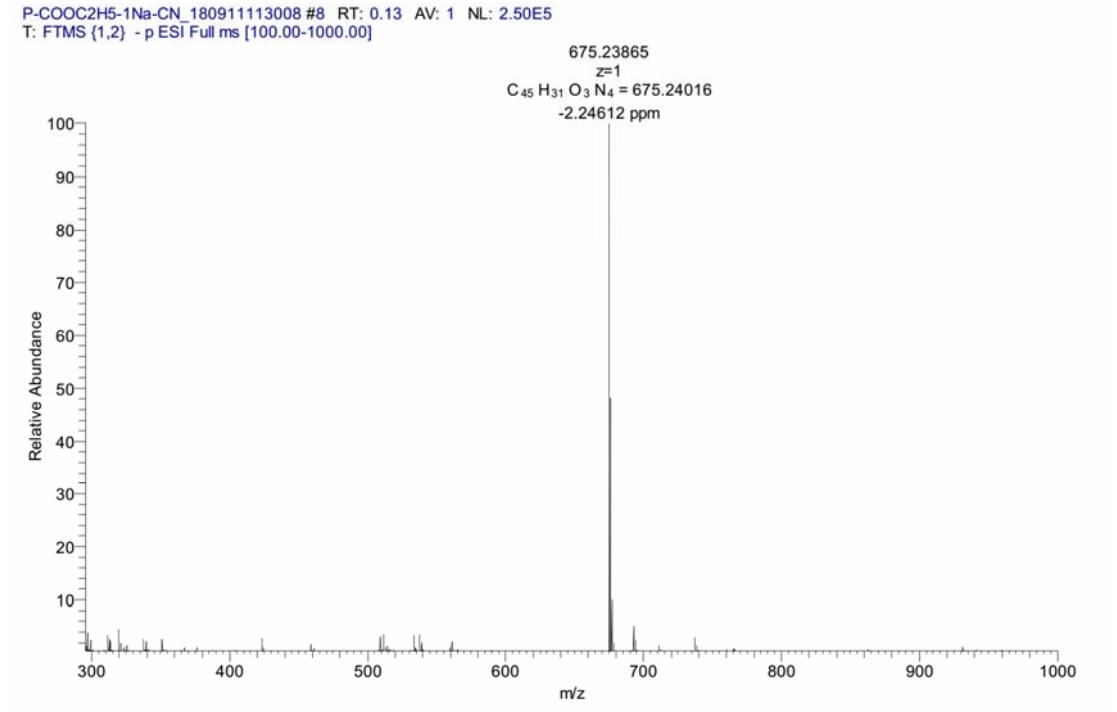


Figure S36. HR-MS spectrum of **MAP2-FE**.

MAP3-FE: The yield gives 65.4%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 8.07 (d, *J* = 15.6Hz, 1H), 7.93 (s, 1H), 7.91-7.72 (m, 9H), 7.62 (s, 1H), 7.58-7.44 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.21-7.06 (m, 3H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.64 (s, 6H), 1.24 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ = 178.24, 176.54, 165.25, 143.07, 142.86, 141.75, 138.41, 133.08, 132.87, 132.81, 132.46, 131.10, 130.43, 130.00, 129.67, 128.86, 128.37, 128.33, 128.19, 128.04, 127.73, 127.68, 127.27, 127.23, 126.63, 122.42, 113.64, 112.70, 112.63, 112.53, 109.28, 99.15, 93.43, 61.54, 52.76, 25.32, 14.47. HR-MS (ESI, *m/z*) Calcd for $C_{45}H_{32}N_4O_3$ $[M+H]^+$: 677.2547, found: 675.2539, error -1.29 ppm.

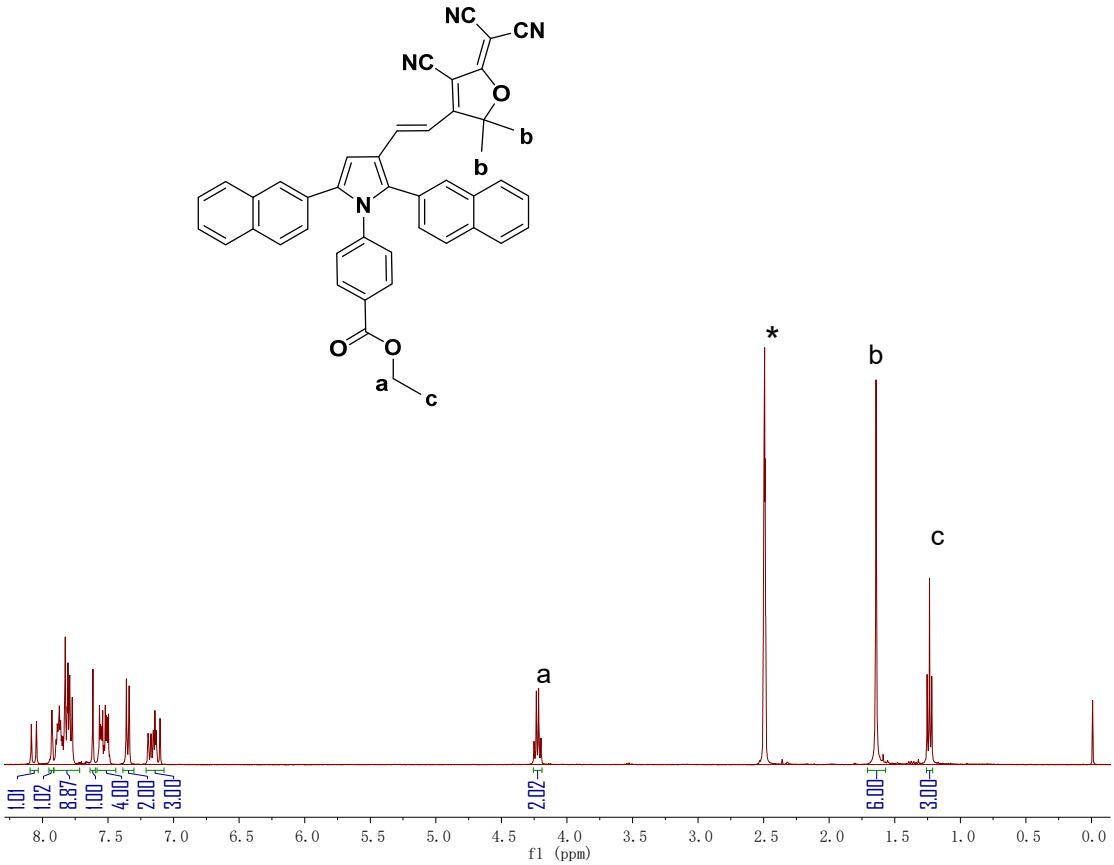


Figure S37. ^{1}H NMR spectrum of **MAP3-FE** in DMSO-*d*$_6$.

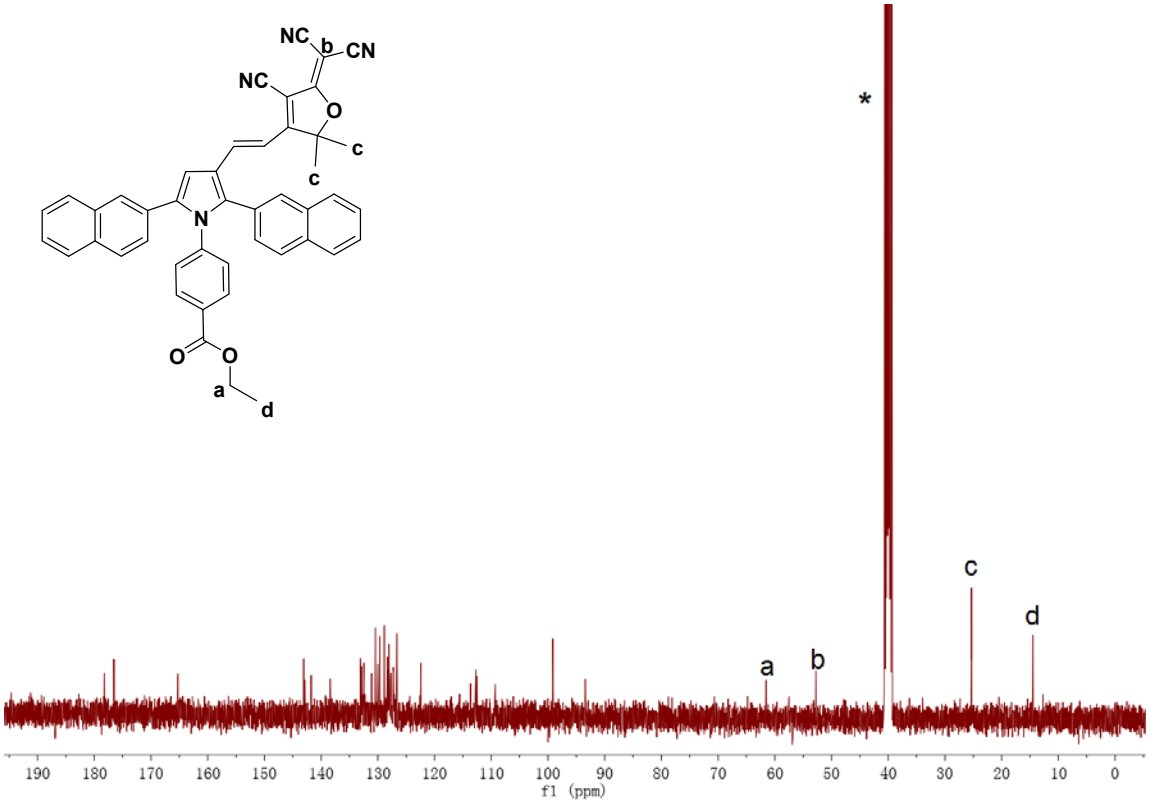


Figure S38. ^{13}C NMR spectrum of **MAP3-FE** in DMSO-*d*$_6$.

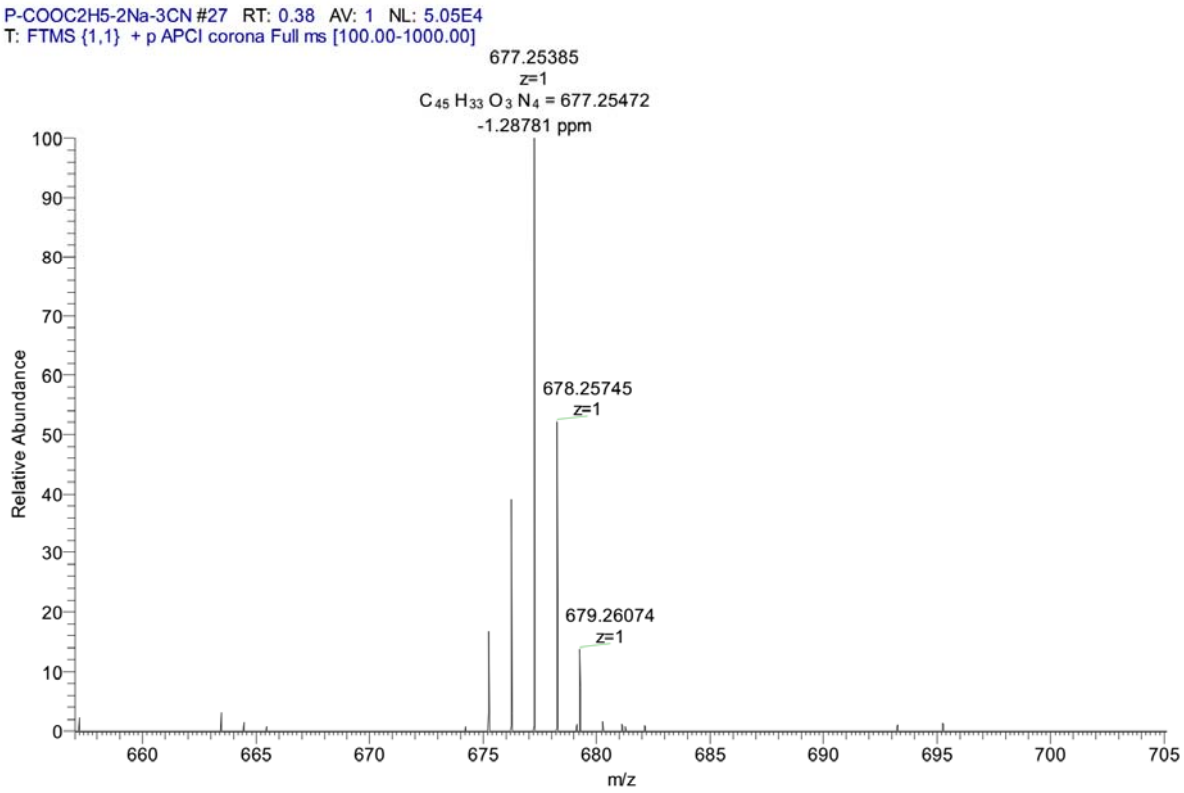


Figure S39. HR-MS spectrum of **MAP2-FE**.

MAP4-FE: The yield gives 37.7%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 8.55 (d, *J* = 9.2Hz, 3H), 8.44 (s, 1H), 8.22-8.04 (m, 6H), 8.01-7.93 (m, 3H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.71 (s, 1H), 7.61-7.49 (m, 4H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 9.2 Hz, 1H), 7.17 (d, *J* = 15.6 Hz, 1H), 7.13 (d, *J* = 9.6 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.67 (s, 6H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ = 178.20, 176.41, 165.23, 143.24, 142.81, 141.82, 138.44, 132.37, 132.11, 132.06, 131.64, 131.10, 130.80, 130.58, 130.52, 130.45, 130.03, 129.57, 128.55, 128.29, 128.05, 127.57, 126.96, 126.77, 126.68, 126.52, 126.41, 126.29, 126.15, 122.65, 113.64, 112.68, 112.52, 109.60, 99.13, 93.45, 61.53, 52.79, 25.37, 14.43.HR-MS (EI, *m/z*) Calcd for $C_{53}H_{36}N_4O_3$ $[M]^+$: 776.2782, found: 776.2791, error 1.16 ppm.

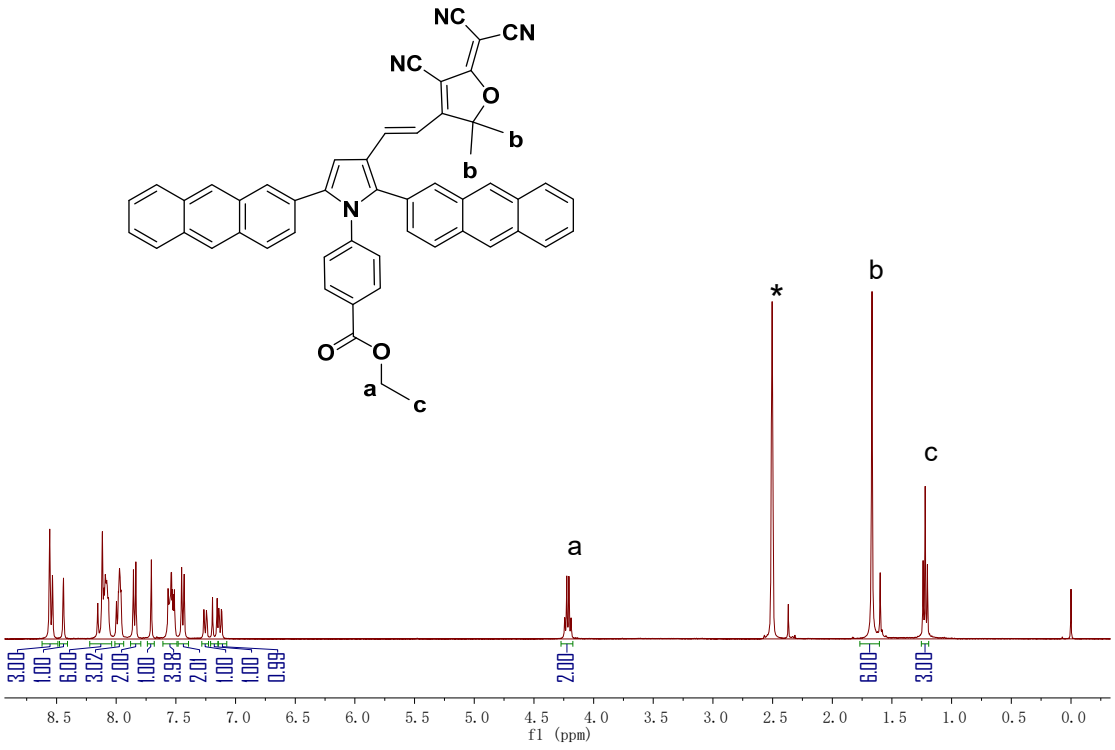


Figure S40. ^{1}H NMR spectrum of **MAP4-FE** in DMSO-*d*$_6$.

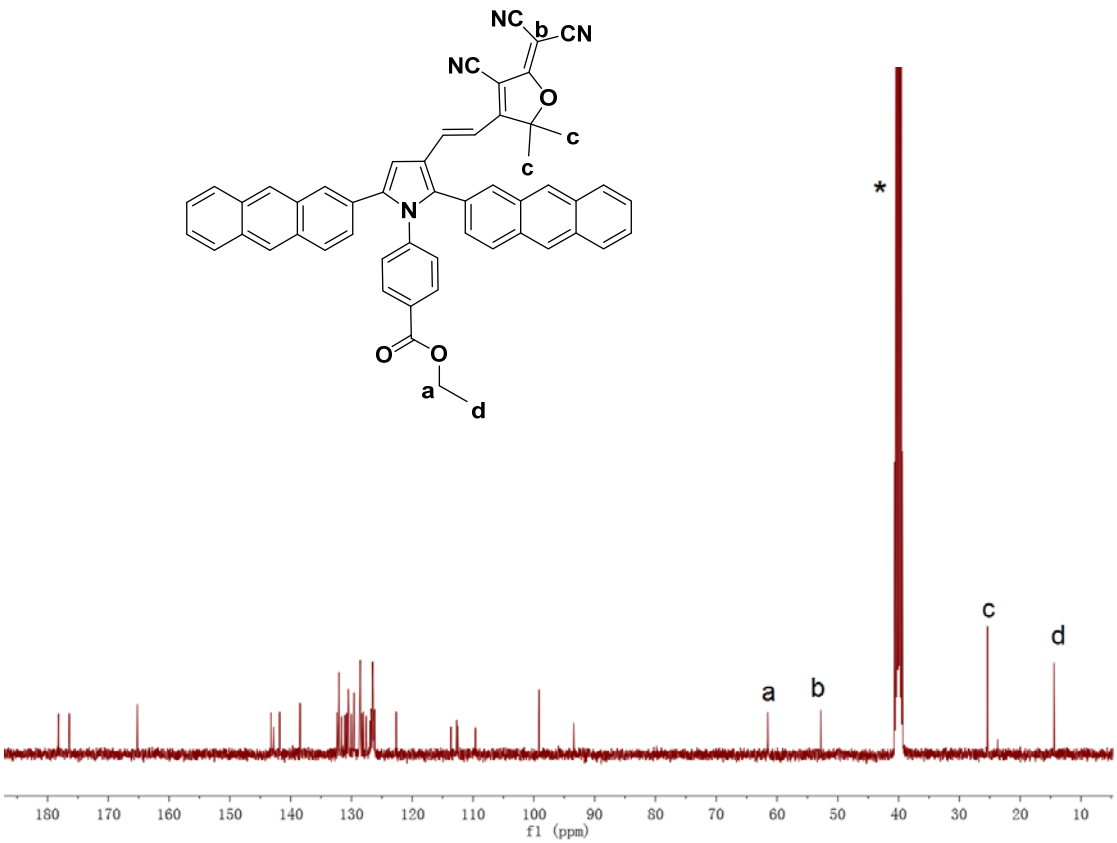


Figure S41. ^{13}C NMR spectrum of **MAP4-FE** in DMSO-*d*$_6$.

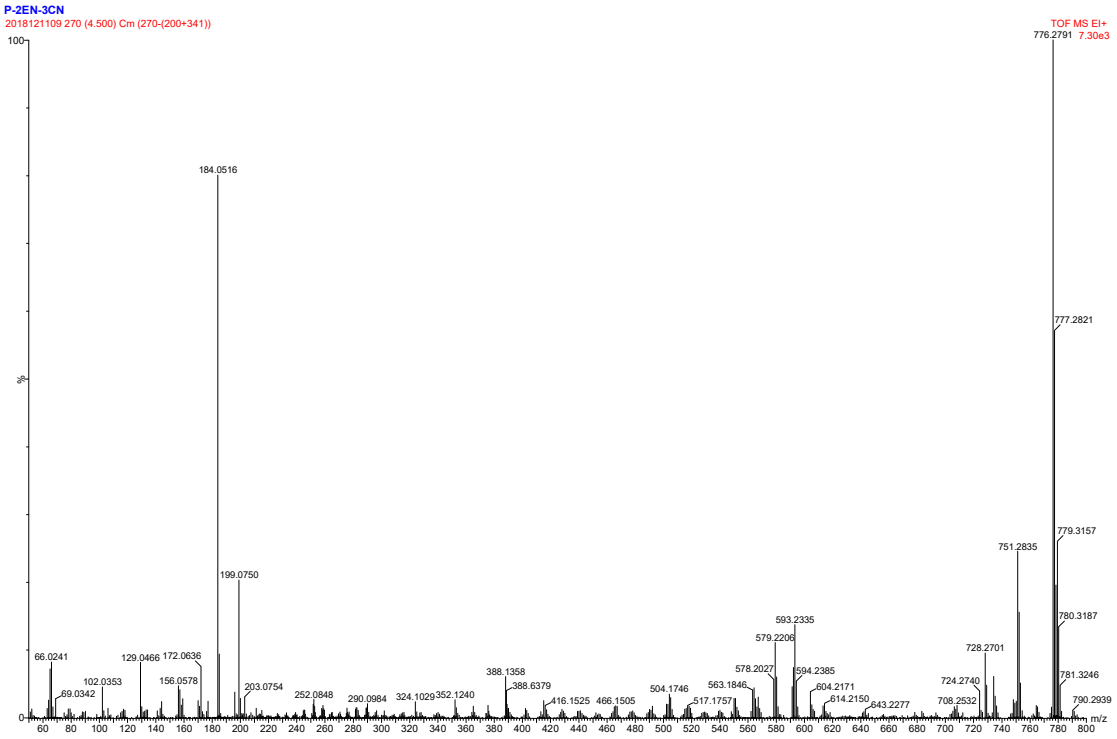


Figure S42. HR-MS spectrum of **MAP4-FE**.

MAP5-FE: The yield gives 73.2%. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.76 (s, 1H), 8.70 (s, 1H), 8.21-8.05 (m, 6H), 7.94 (d, J = 8.4Hz, 2H), 7.75 (s, 1H), 7.72-7.63 (m, 4H), 7.61-7.49 (m, 5H), 7.05 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 16.0 Hz, 1H), 6.78 (d, J = 8.4 Hz, 2H), 3.90 (q, J = 8.4 Hz, 2H), 1.44 (s, 6H), 0.98 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 178.06, 175.65, 164.54, 141.82, 141.07, 138.59, 134.11, 132.27, 131.94, 131.04, 131.01, 130.32, 129.45, 129.40, 129.21, 129.15, 128.28, 127.72, 126.32, 126.07, 125.44, 125.14, 124.32, 122.59, 113.50, 112.58, 112.47, 111.78, 98.96, 93.96, 61.17, 52.88, 25.11, 14.16. HR-MS (EI, *m/z*) Calcd for $C_{53}H_{36}N_4O_3$ $[M]^+$: 776.2782, found: 776.2781, error -0.13 ppm.

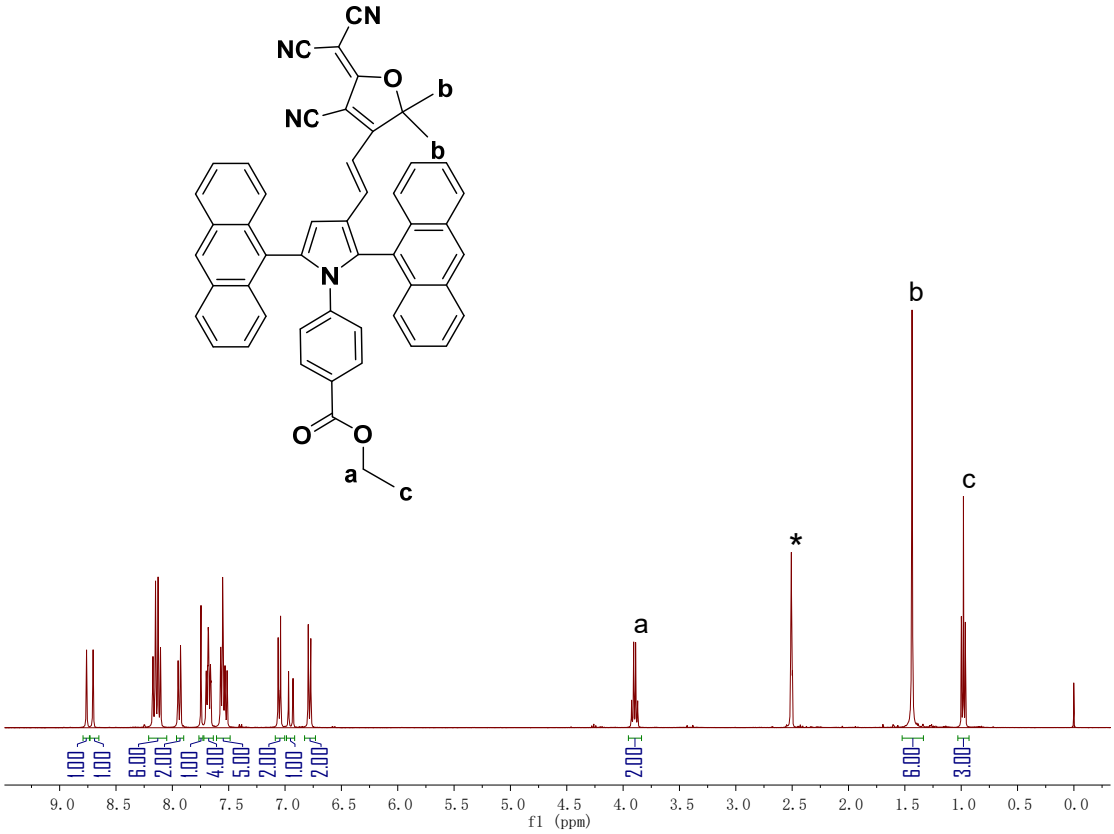


Figure S43. ^{1}H NMR spectrum of **MAP5-FE** in DMSO-d_6.

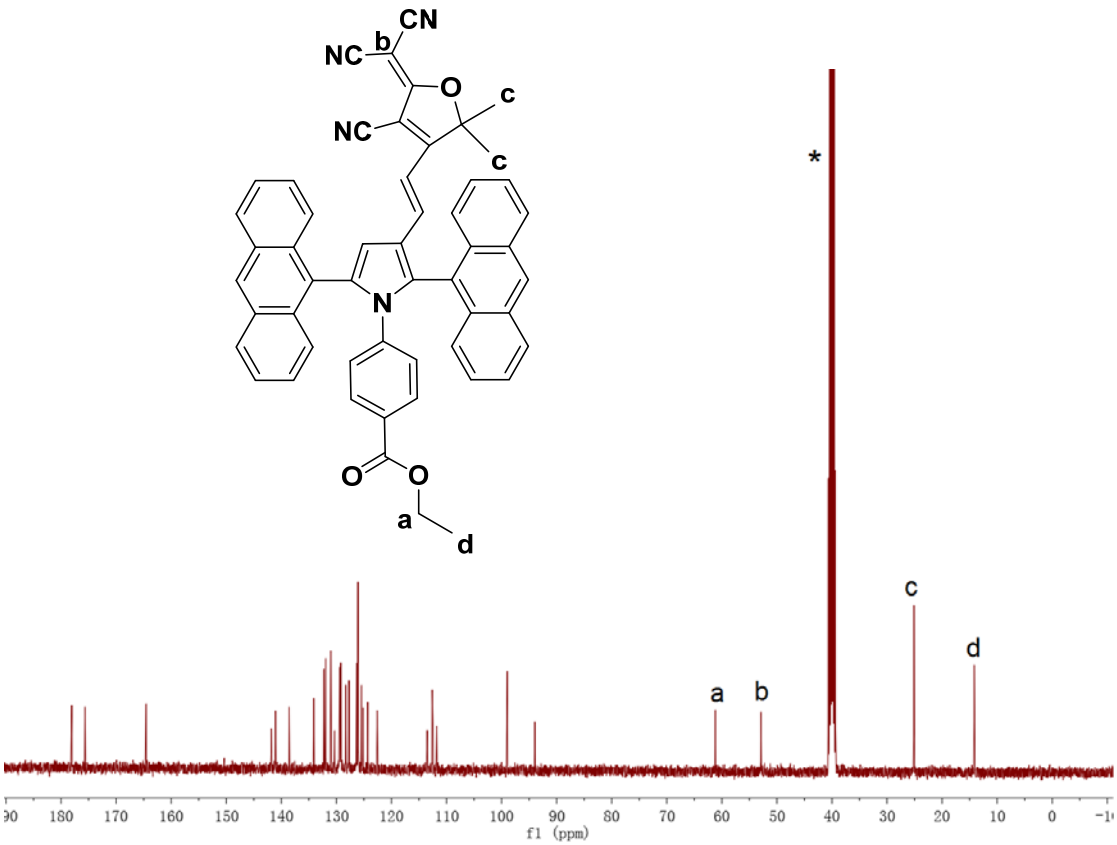


Figure S44. ^{13}C NMR spectrum of **MAP5-FE** in DMSO-*d*$_6$.

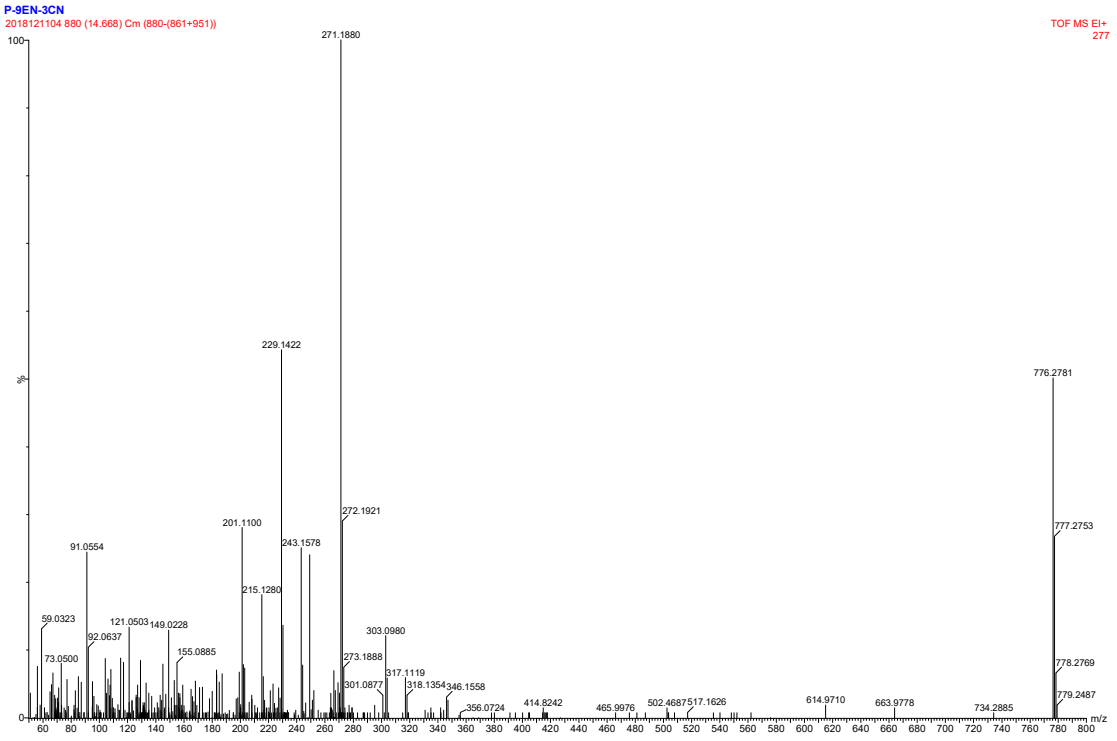


Figure S45. HR-MS spectrum of **MAP5-FE**.

MAP6-FE: The yield gives 81.9%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 8.43-8.31 (m, 6H), 8.30-8.08 (m, 11H), 8.05 (d, *J* = 9.2Hz, 1H), 7.83 (d, *J* = 16.0Hz, 1H),7.74 (s, 1H), 7.32 (d, *J* = 8.4Hz, 2H), 7.22 (d, *J* = 8.4Hz, 2H), 7.08 (d, *J* = 16.0Hz, 1H), 3.91 (q, *J* = 7.2 Hz, 2H), 1.55 (s, 3H), 1.51 (s, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ = 178.10, 176.12, 164.75, 142.71, 141.66, 141.33, 136.70, 131.97, 131.34, 131.23, 131.17, 130.79, 130.65, 130.25, 129.54, 129.23, 128.96, 128.61, 128.43, 127.73, 127.13, 126.49, 126.28, 126.04, 125.41, 125.05, 124.82, 124.14, 124.08, 123.92, 123.79, 113.56, 112.55, 112.43, 112.07, 111.36, 98.99, 93.48, 61.14, 52.71, 25.26, 23.69, 14.14. HR-MS (APCI, *m/z*) Calcd for $C_{57}H_{36}N_4O_3$ $[M+H]^+$: 825.2860, found: 825.2858, error -0.23 ppm.

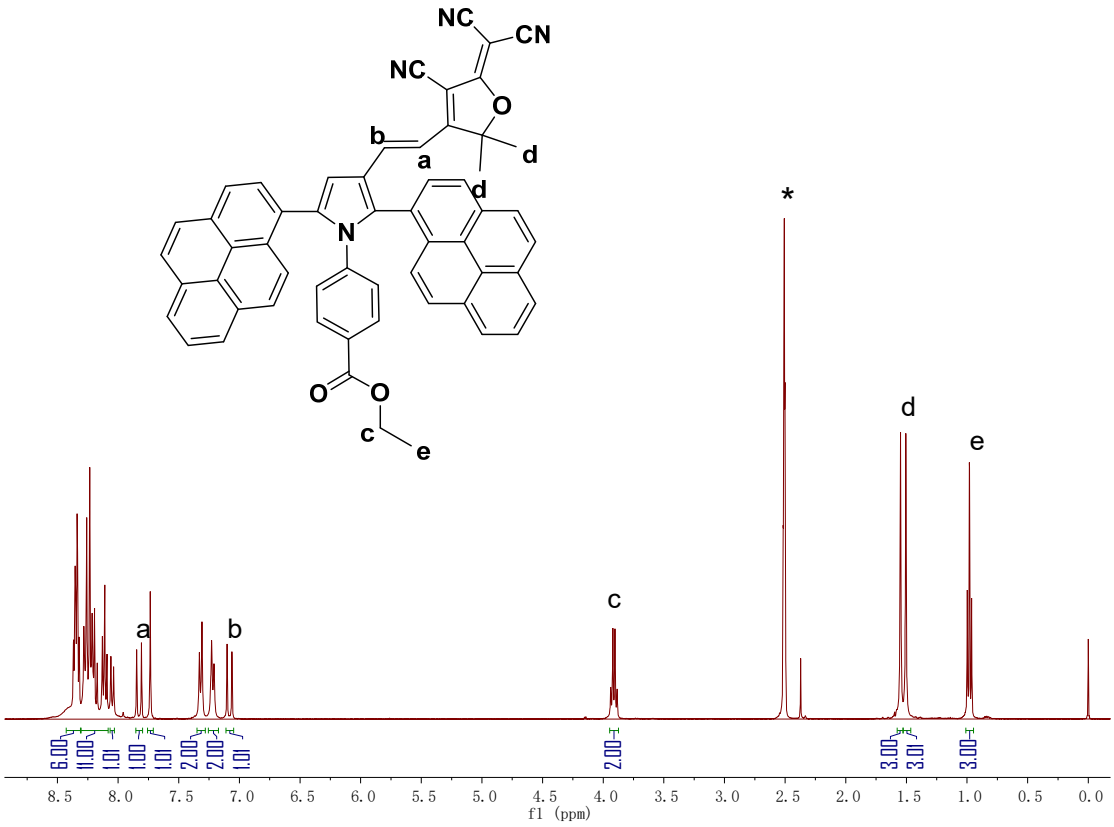


Figure S46. ^{1}H NMR spectrum of **MAP5-FE** in DMSO-*d*$_6$.

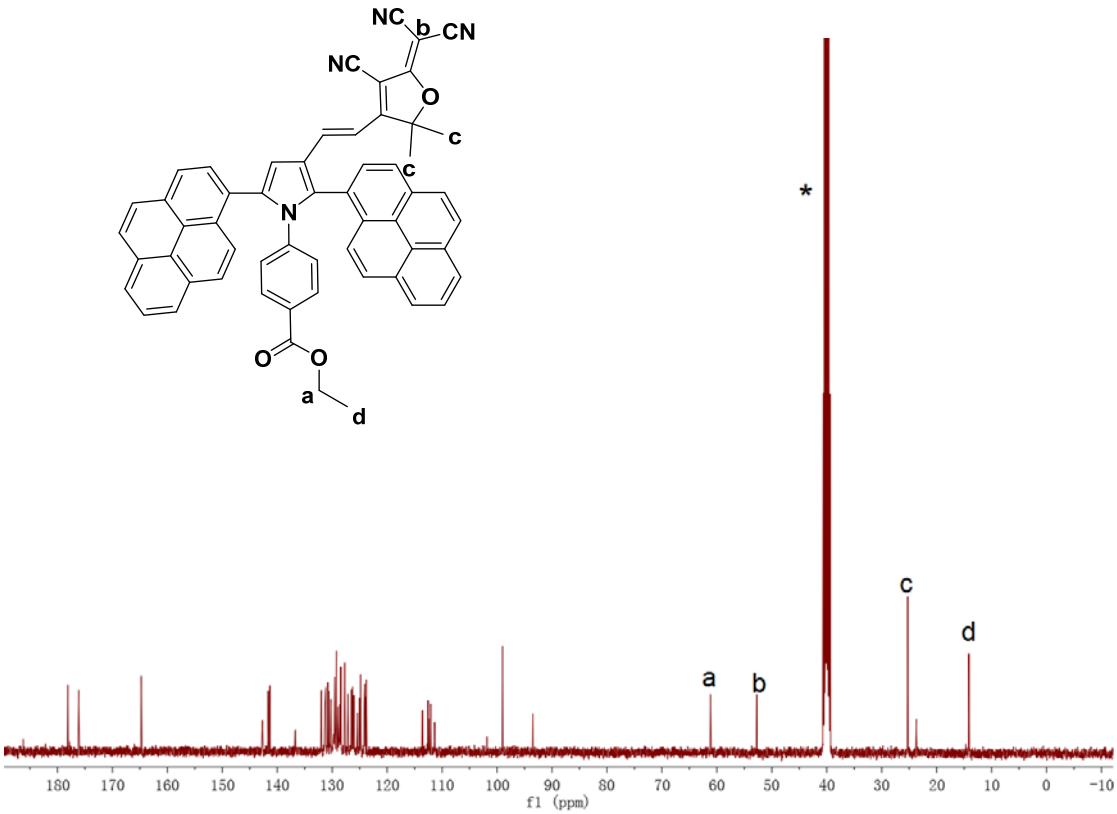


Figure S47. ^{13}C NMR spectrum of **MAP6-FE** in DMSO-*d*$_6$.

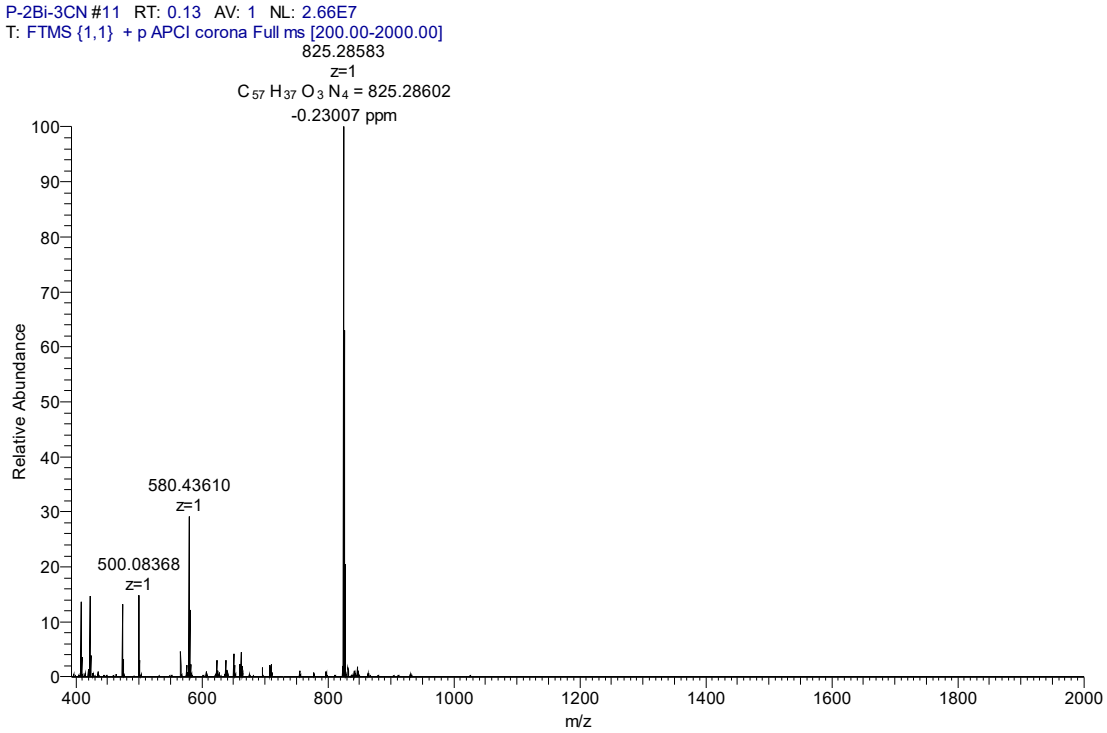


Figure S48. HR-MS spectrum of **MAP6-FE**.

2. UV and PL spectra of MAPs and MAPs-FE.

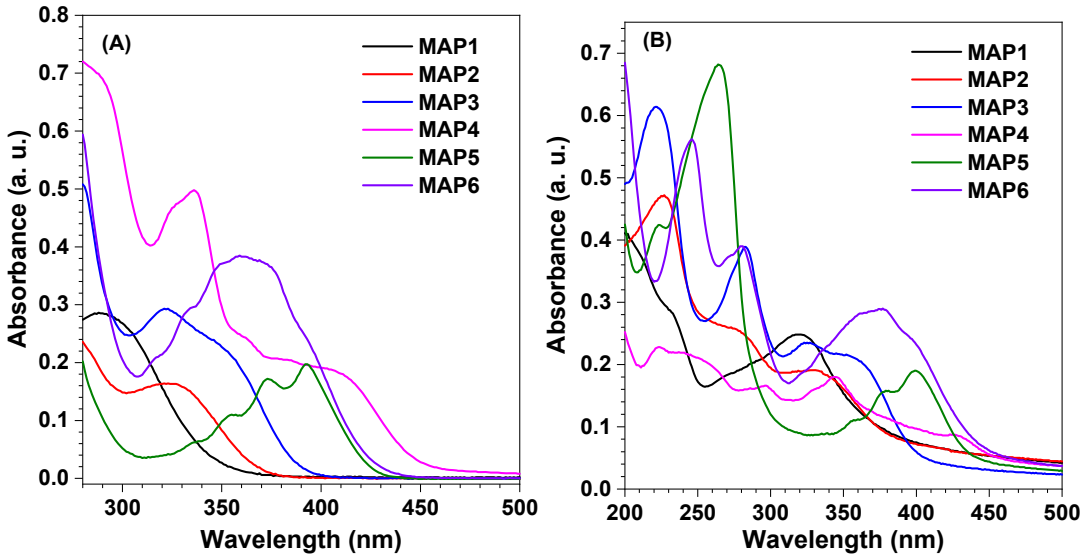


Figure S49. (A) Absorption spectra of **MAP1~6** in DMSO solution (1.0×10^{-5} mol/L). (B) Absorption spectra of **MAP1~6** in film.

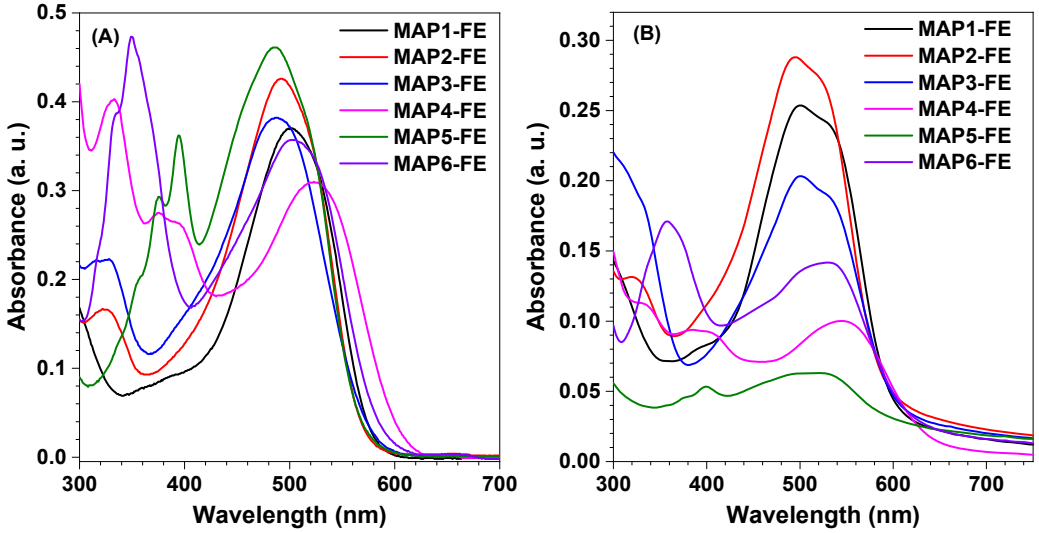


Figure S50. (A) Absorption spectra of **MAP1~6-FE** in DMSO solution [1.0×10^{-5} mol/L]. (B) Absorption spectra of **MAP1~6-FE** in film.

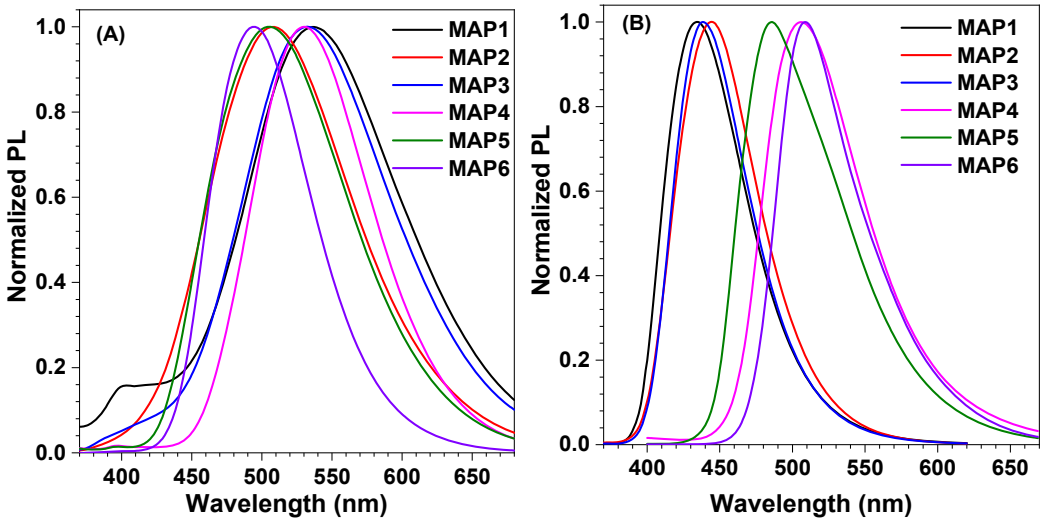


Figure S51. Normalized PL spectra of**MAP1~6** in DMSO solution (A) and in powder state (B). Excited wavelength (λ_{ex}): 350 nm for **MAP1**, 340 nm for **MAP2**, 340 nm for **MAP3**, 350 nm for **MAP4**, 350 nm for **MAP5**, and 350 nm for **MAP6**.

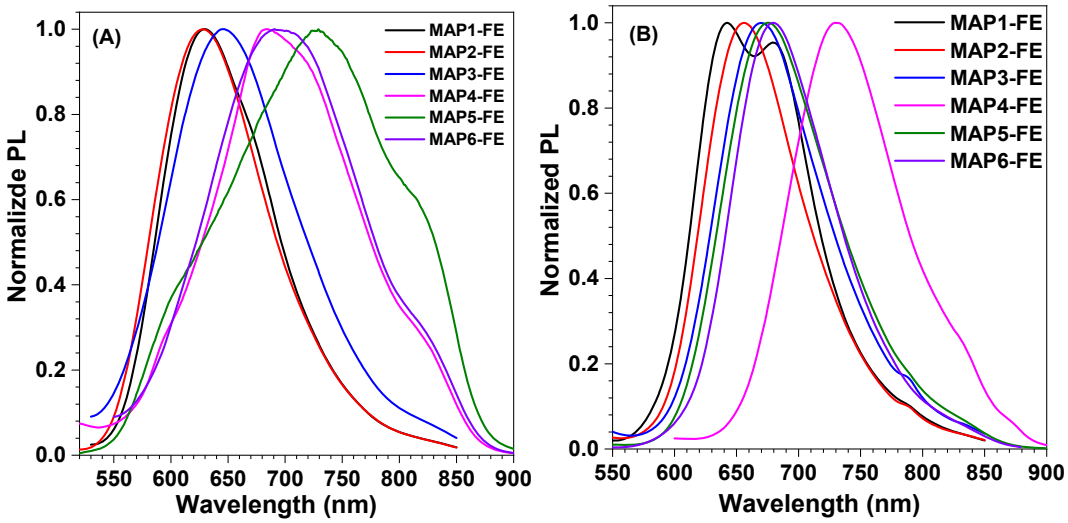


Figure S52. Normalized PL spectra of **MAP1~6-FE** in DMSO solution (A) and in powder state (B). λ_{ex}: 450 nm for **MAP1-FE**, 450 nm for **MAP2-FE**, 450 nm for **MAP3-FE**, 500 nm for **MAP4-FE**, 460 nm for **MAP5-FE**, and 510 nm for **MAP6-FE**.

3. Photophysical property data of compounds MAPs and MAPs-FE.

Table S1. Photophysical property data of compounds **MAP1~6**.[a]

Compounds	λ_{abs} (nm)[b]			λ_{em} (nm)[c]		
	In THF	In DMSO	In Film	In THF	In DMSO	In Powder
MAP1	285	289	318	479	536	435
MAP2	325	325	329	447	507	445
MAP3	318	322	324	478	533	438
MAP4	334	336	345	495	530	506
MAP5	390	392	399	464	505	486
MAP6	360	359	377	470	494	509

Notes: [a] [**MAP1~6**] = 1.0×10^{-5} mol/L. [b] The longest peak value. [c] The main peak value.

Table S2. Photophysical property data of compounds **MAP1~6-FE**.[a]

Compounds	λ_{abs} (nm)[b]			λ_{em} (nm)[c]		
	In THF	In DMSO	In Film	In THF	In DMSO	In Powder
MAP1-FE	484	500	501	601	631	642
MAP2-FE	478	493	496	605	629	656
MAP3-FE	485	487	501	613	646	670
MAP4-FE	507	523	546	665	685	729
MAP5-FE	475	485	524	657	729	676
MAP6-FE	488	503	534	660	691	679

Notes: [a] [**MAP1~6-FE**] = 1.0×10^{-5} mol/L. [b] The longest peak value. [c] The main peak value.

4. Solvatochromic properties of MAPs and MAPs-FE.

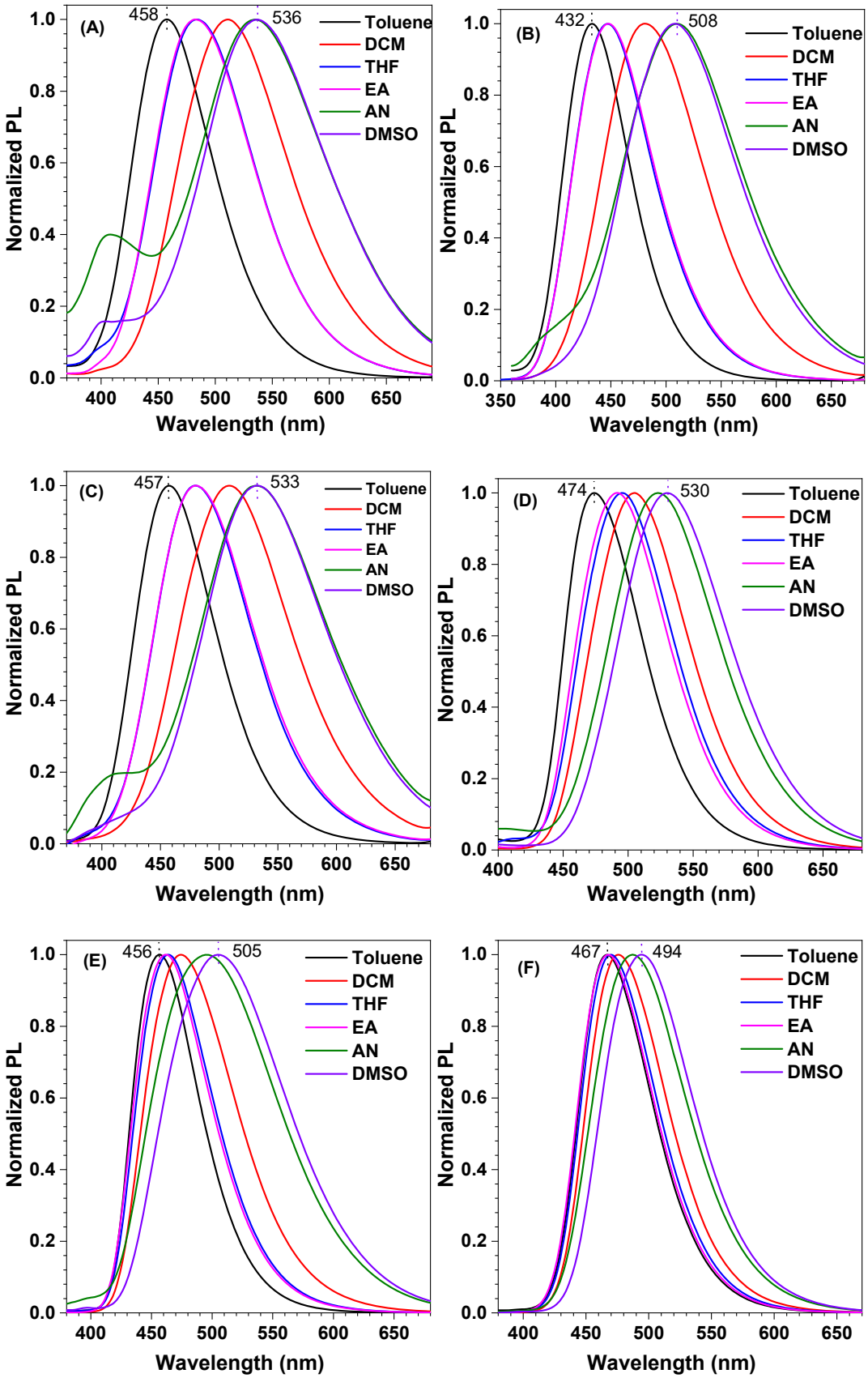
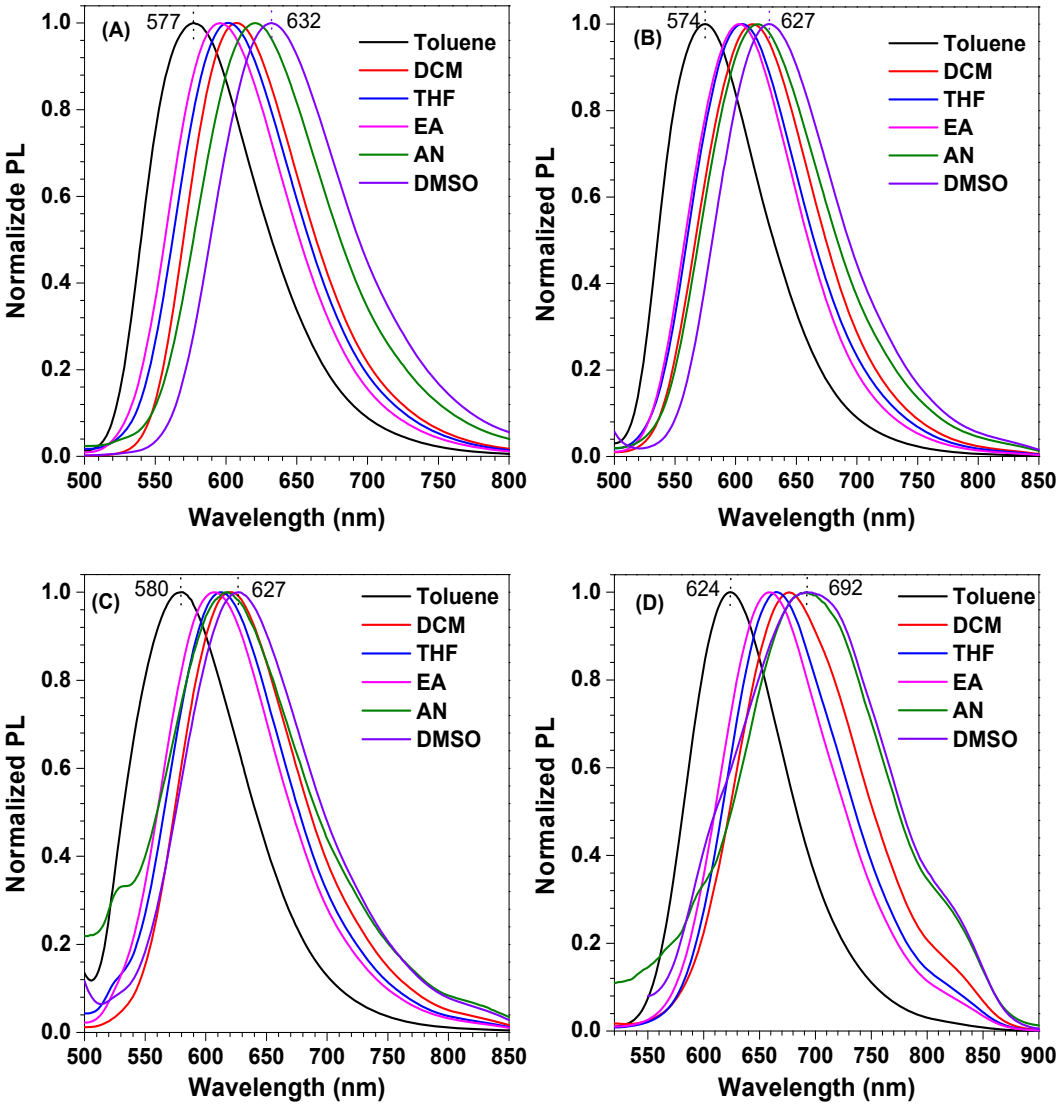


Figure S53. Normalized PL spectra of **(A) MAP1** (λ_{ex} = 350 nm), **(B) MAP2** (λ_{ex} = 340 nm), (C) **MAP3** (λ_{ex} = 340 nm), (D) **MAP4** (λ_{ex} = 350 nm), (E) **MAP5** (λ_{ex} = 350 nm) **and (F) MAP6** (λ_{ex} = 350 nm) in different solvents.



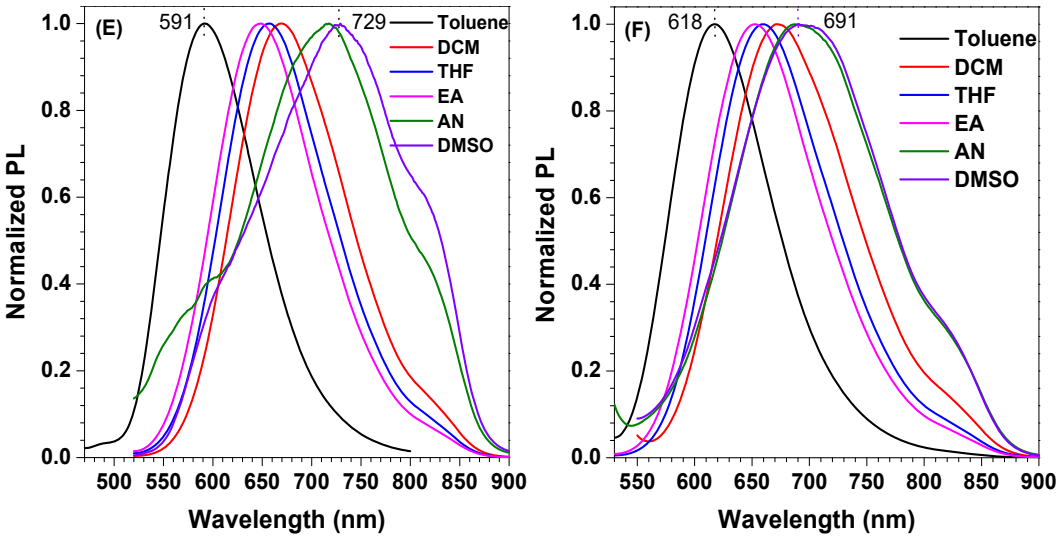


Figure S54. Normalized PL spectra of (A) **MAP1-FE** (λ_{ex} = 450 nm), (B) **MAP2-FE** (λ_{ex} = 450 nm), (C) **MAP3-FE** (λ_{ex} = 450 nm), (D) **MAP4-FE** (λ_{ex} = 500 nm), (E) **MAP5-FE** (λ_{ex} = 460 nm) and (F) **MAP6-FE** (λ_{ex} = 510 nm) in different solvents.

Table S3. The maximum PL emission wavelength (λ_{max}) of **MAP1~6** and **MAP1~6-FE** in different solvents.

Compounds	**λ_{max} in different solvents (nm)**						**$\Delta\lambda$ (nm)**
	Toluene	DCM	THF	EA	AN	DMSO	
MAP1	458	510	479	482	534	536	78
MAP2	432	480	447	448	508	507	75
MAP3	457	509	478	480	532	533	76
MAP4	474	505	495	491	523	530	56
MAP5	456	474	464	461	495	505	49
MAP6	467	476	470	468	487	494	27
MAP1-FE	577	607	601	595	620	631	54
MAP2-FE	574	614	605	603	618	629	55
MAP3-FE	580	620	613	607	617	646	66
MAP4-FE	624	676	665	658	691	685	61
MAP5-FE	591	669	657	649	718	729	138
MAP6-FE	618	671	660	652	687	691	73

Note: $\Delta\lambda$ means the net change of λ_{max} from DMSO to toluene.

5. The aggregation PL property of MAPs and MAPs-FE.

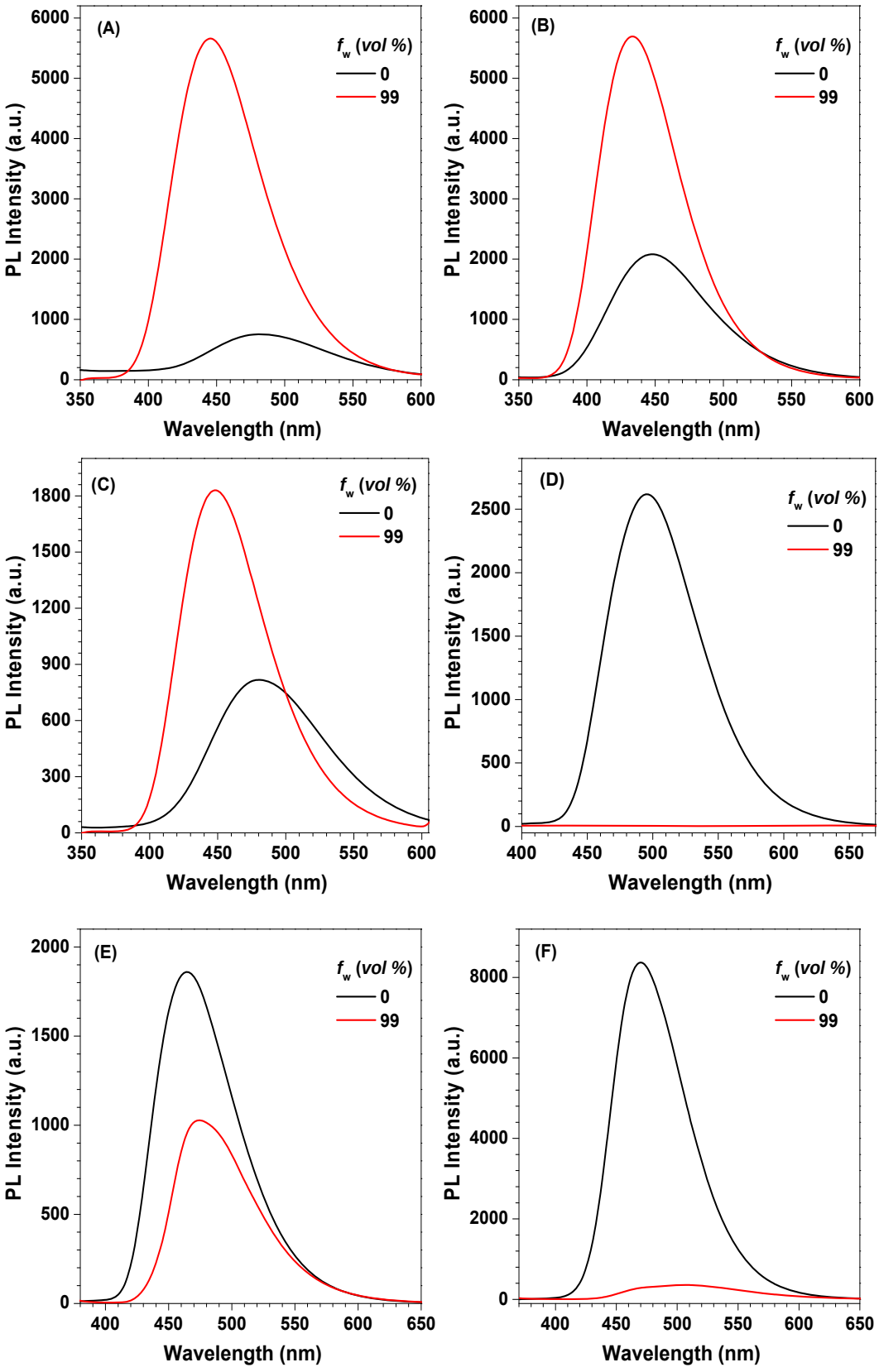
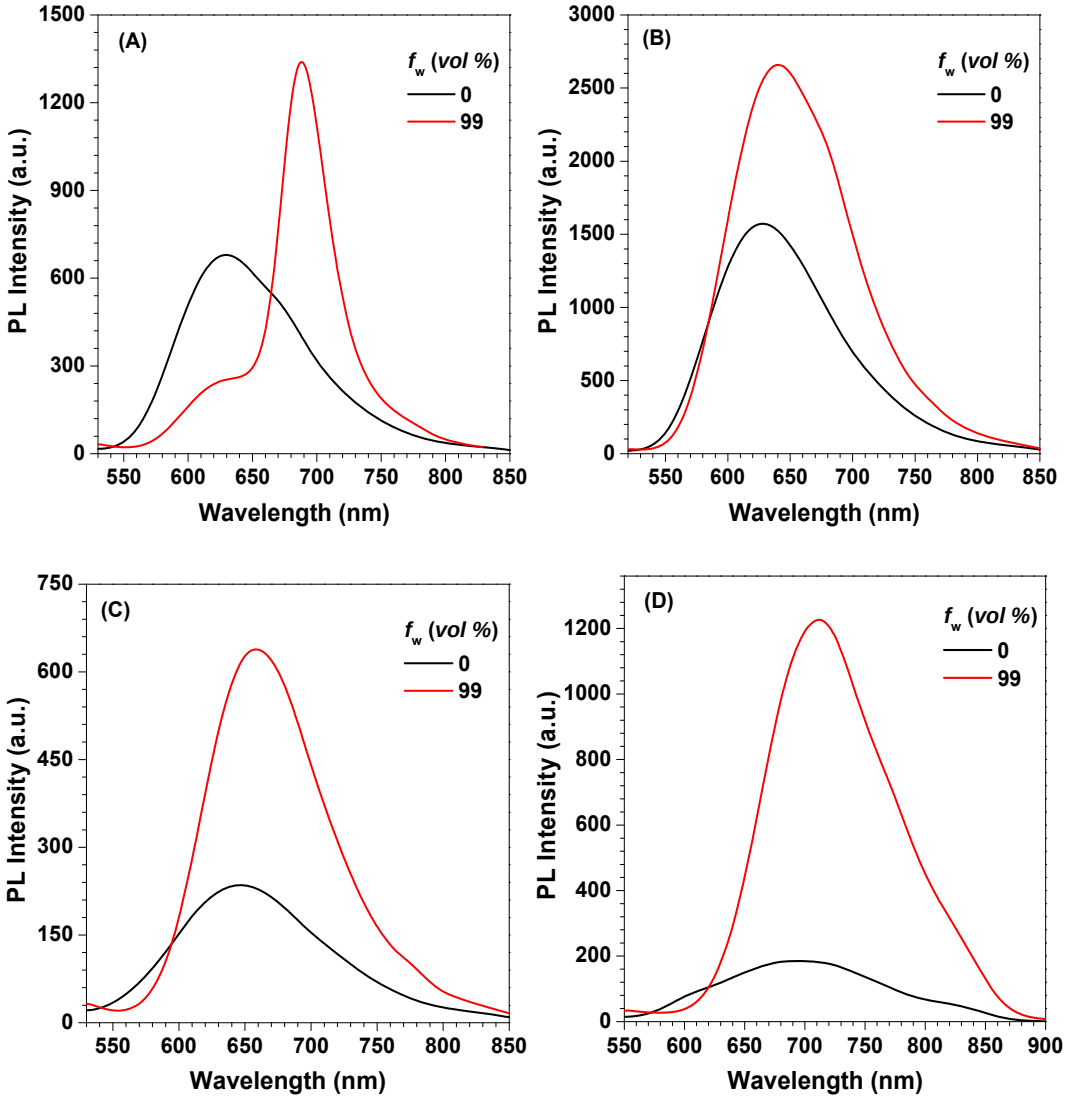


Figure S55. PL spectra of (A) **MAP1**, (B) **MAP2**, (C) **MAP3**, (D) **MAP4**, (E) **MAP5**, (F) **MAP6** in THF solution and the mixture of THF/H_2O with 99% water fractions (f_w).



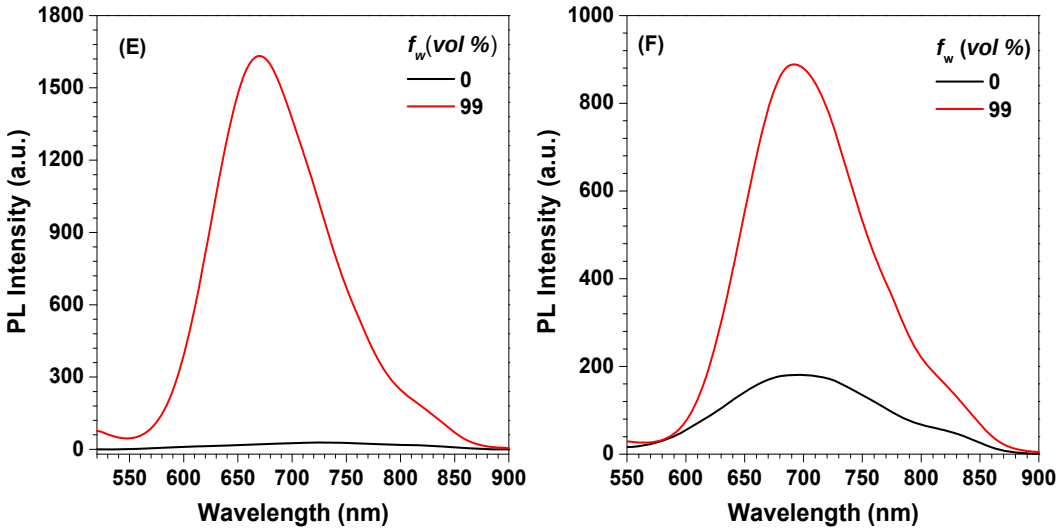
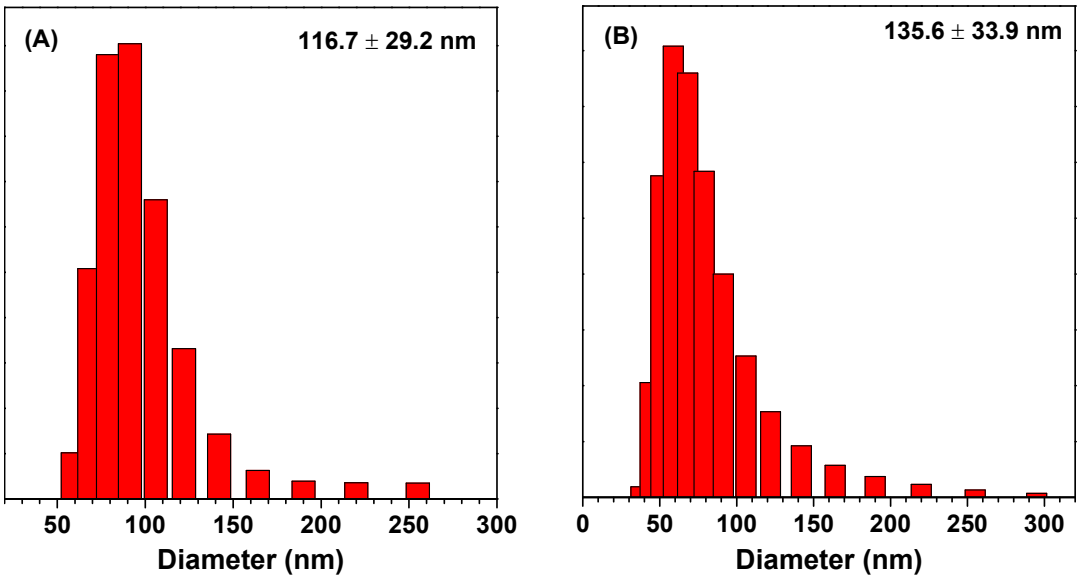


Figure S56. PL spectra of (A) **MAP1-FE**, (B) **MAP2-FE**, (C) **MAP3-FE**, (D) **MAP4-FE**, (E) **MAP5-FE**, (F) **MAP6-FE** in DMSO solution and the mixture of DMSO/H_2O with f_w = 99%.

6. The dynamic light scattering data of MAPs and MAPs-FE.



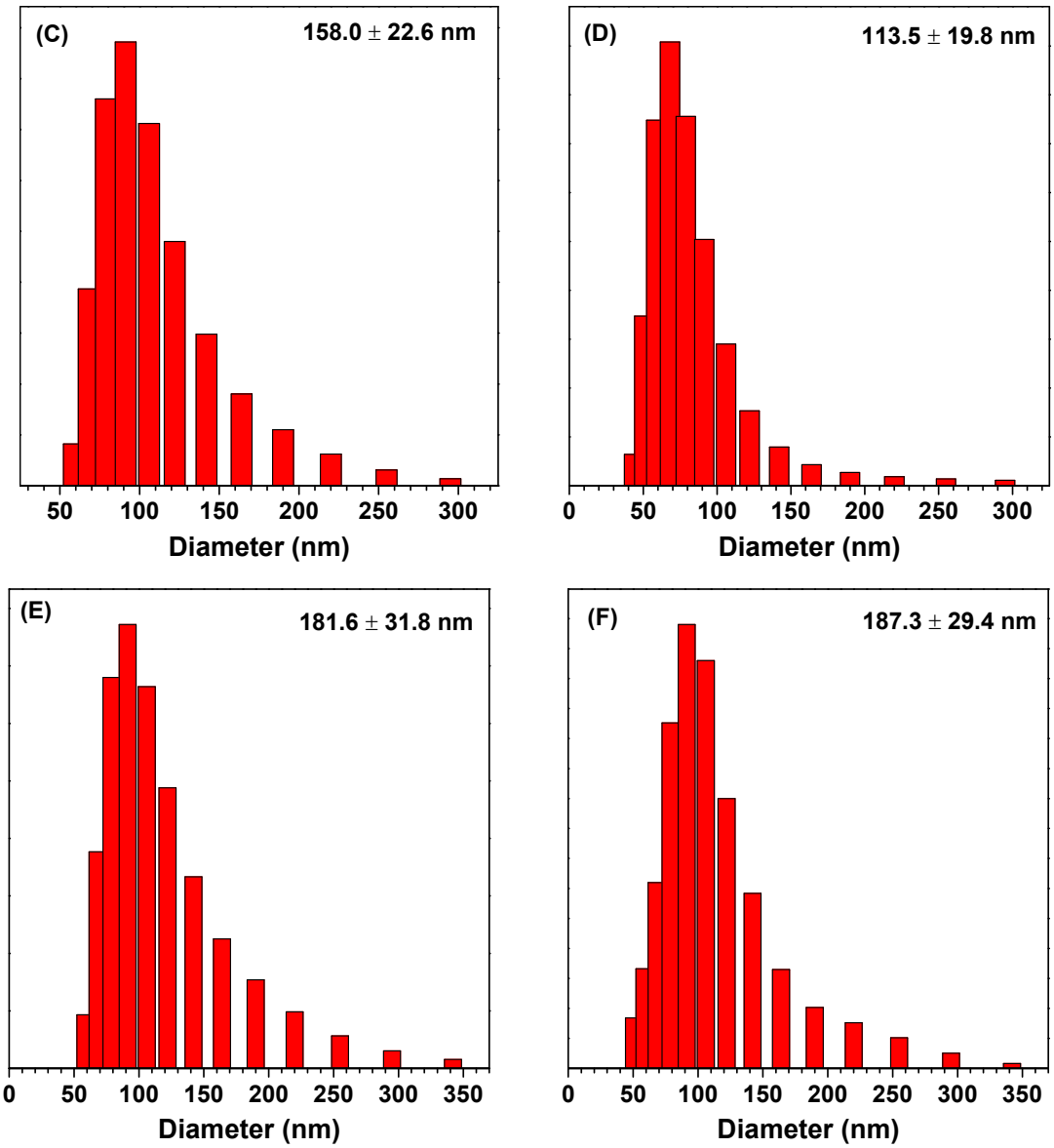


Figure S57. Particle diameter size distributions of (A) **MAP1**, (B) **MAP2,** (C) **MAP3**, (D) **MAP4**, (E) **MAP5** and (F) **MAP6** in THF/water (1:99). [**MAP1**] = [**MAP2**] = [**MAP3**] = [**MAP4**] = [**MAP5**] = [**MAP6**] = 1.0×10^{-5} mol/L.

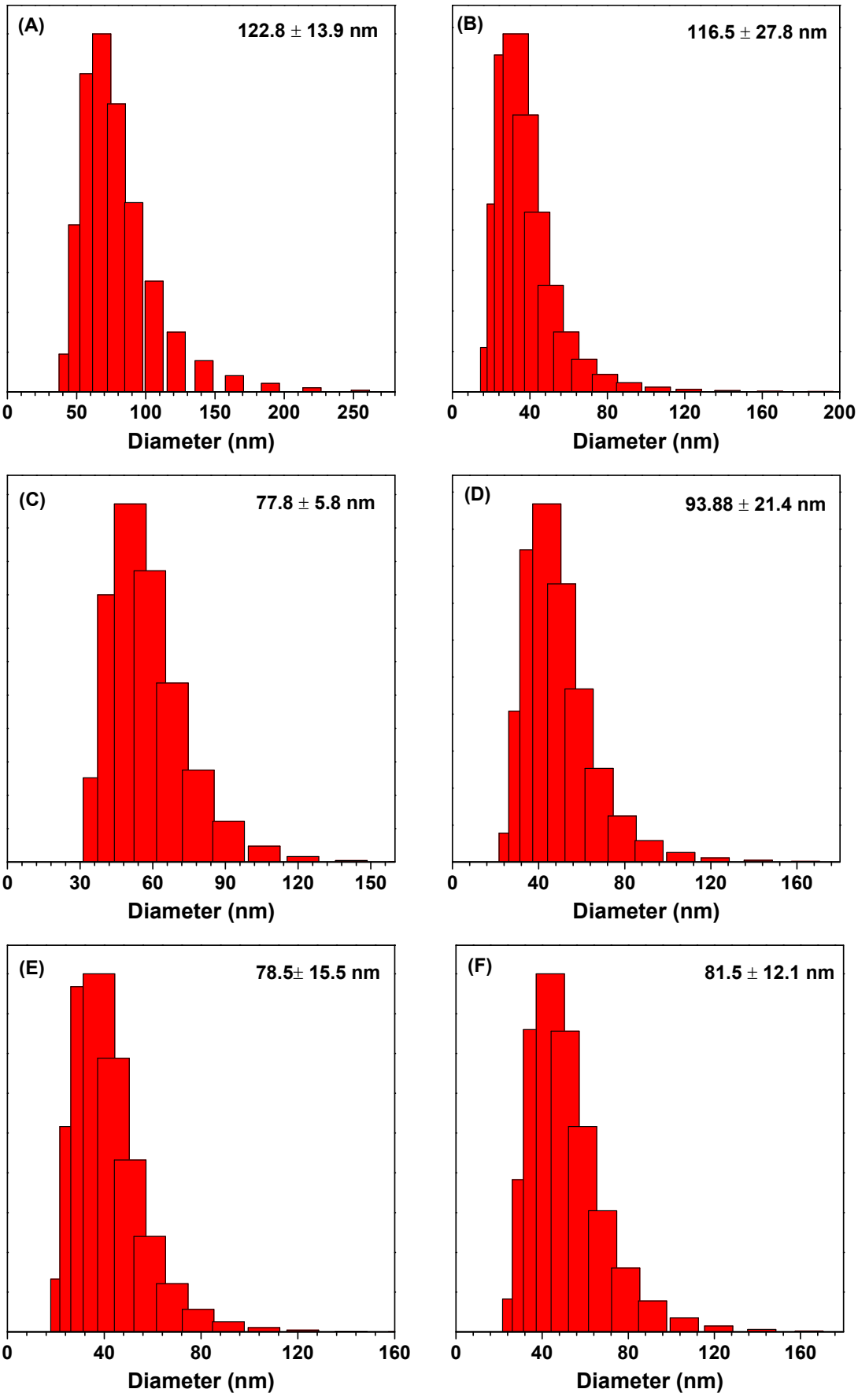

(A)
122.8 ± 13.9 nm
0
50
100
150
200
250
Diameter (nm)
(B)
116.5 ± 27.8 nm
0
40
80
120
160
200
Diameter (nm)
(C)
77.8 ± 5.8 nm
0
30
60
90
120
150
Diameter (nm)
(D)
93.88 ± 21.4 nm
0
40
80
120
160
Diameter (nm)
(E)
78.5± 15.5 nm
0
40
80
120
160
Diameter (nm)
(F)
81.5 ± 12.1 nm
0
40
80
120
160
Diameter (nm)

Figure S58. Particle diameter size distributions of (A) **MAP1-FE**, (B) **MAP2-FE**, (C) **MAP3-FE**, (D) **MAP4-FE**, (E) **MAP5-FE** and (F) **MAP6-FE** in DMSO/water (1:99). [**MAP1-FE**] = [**MAP2-FE**] = [**MAP3-FE**] = [**MAP4-FE**] = [**MAP5-FE**] = [**MAP6-FE**] = 1.0×10^{-5} mol/L.

Table S4. The absolute quantum yield and fluorescence lifetime of **MAP1~6** in solution and solid.

Comp-ounds	Solution						Solid					
	λ_{ex}[b] (nm)	Φ_F (%)	λ_{em}[c] (nm)	τ (ns)	k_r[d] ($\times10^8$ s^{-1})	k_{nr}[e] ($\times10^8$ s^{-1})	λ_{ex} (nm)	Φ_F (%)	λ_{em} (nm)	τ (ns)	k_r ($\times10^8$ s^{-1})	k_{nr} ($\times10^8$ s^{-1})
MAP1	350	1.92	479	3.57	0.0538	2.747	350	25.04	435	10.48	0.2389	0.715
MAP2	340	13.19	447	4.76	0.2771	1.824	340	38.46	445	4.02	0.9567	1.531
MAP3	340	4.31	478	4.07	0.1059	2.351	340	22.64	438	2.30	0.9843	3.363
MAP4	350	49.15	495	3.62	1.3577	1.405	350	3.89	506	0.85	0.4576	11.307
MAP5	350	58.58	464	2.63	2.2274	1.575	350	12.35	486	1.73	0.7139	5.066
MAP6	350	90.86	470	1.84	4.9380	0.497	350	36.73	509	1.53	2.4007	4.135

Note: [a] Measured in THF at [MAPs] = 1.0×10^{-5} mol/L. [b] The excitation wavelength (λ_{ex}) for obtaining the absolute fluorescence quantum yield (Φ_F) by integrating sphere. [c] The emission wavelength (λ_{em}) for obtaining the fluorescence lifetime (τ). [d] Radiative rate (k_r). [e] Nonradiative rate (k_{nr}).

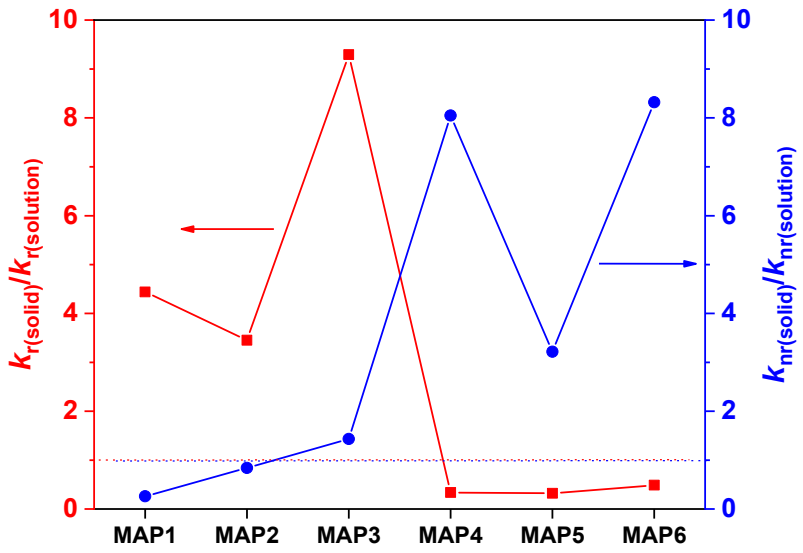


Figure S59. The change of k_r and k_{nr} of MAPs from solution to solid.

7. References

1. Y.-R. Wang, L. Feng, L. Xu, Y. Li, D.-D. Wang, J. Hou, K. Zhou, Q. Jin, G.-B. Ge, J.-N. Cui and L. Yang, *Chem. Commun.*, 2016, **52**, 6064-6067.
2. F. Ren, P. Liu, Y. Gao, J. Shi, B. Tong, Z. Cai and Y. Dong, *Mater. Chem. Front.*, 2019, **3**, 57-63.