Electronic Supplementary Information (ESI) for

Tetrasubstituted Imidazole Derivatives and Their Imidazolium: Photophysical Properties in Aggregate State and Application in Adenosine Detection

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1 General

1.1 Materials

Unless otherwise specified, all chemicals and regents were purchased from commercial source and used directly without further purification. Benzil, phenanthrenequinone and iodomethane were purchased from Tianjin Heowns. Silver fluoride and Silver hexafluorophosphate were purchased from Macklin. Silver tetrafluoroborate was purchased from Energy Chemical. Silver perchlorate was purchased from 9 Ding Chemistry.

1.2 Instruments

NMR spectra were obtained on a Bruker AVANCEIII 400MHz NMR spectrometer. ESI-MS spectra were recorded on an Thermo Q-Exactive. UV-vis spectra were collected by a TU-1901 double beam UV-vis spectrophotometer. Fluorescence spectra was obtained on a Hitachi F-7000 fluorescence spectrophotometer. Fluorescence quantum yields (Φ_F) were recorded on a FLS980 Series of Fluorescence Spectrometers. Dynamic light scattering (DLS) was recorded on a Malvern ZEN3600 Zetasizer. Single crystal data were obtained on a Bruker-AXS SMART APEX 2 CCD diffractometer. XRD was collected on XPERT-PRO.

2 Synthesis and characterization

2.1 PI:

A mixture of diphenylethanedione (1.05 g, 5.0 mmol), benzaldehyde (0.53 g, 5.0 mmol), aniline (0.70 g, 7.5 mmol), ammonium acetate (1.93 g, 25.0 mmol) was stirred in acetic acid (40ml) and refluxed for 4 h. The reaction solution was moved to room temperature for cooling, then poured into an ice water mixture to collect solids and washed with an appropriate amount of water. The crude product was recrystallized with ethyl acetate. The product was obtained in 68.1% yield (1.26g) as a faint yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51-7.48 (m, 2H), 7.40-7.37 (m, 2H), 7.34-7.23 (m, 15H), 7.19-7.16 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.46, 137.21,

137.09, 134.79, 131.77, 131.61, 130.82, 130.78, 129.62, 129.23, 128.93, 128.90, 128.82, 128.75, 128.64, 126.97, 126.85. MS (m/z): $[M+H]^+$ calcd for $[C_{27}H_{21}N_2]^+$: 373.17; found: 373.17.

2.2 MPI-I:

A mixture of PI (1.00 g, 2.7 mmol), Methyl iodide (3.83 g, 27.0 mmol), acetonitrile (60 mL) was stirred for 24h at 70°C. After the reaction was completed, the solvent was evaporated under reduced pressure to obtain the crude product. Purification of crude product by column chromatography (eluent, dichloromethane, and gradually increased to dichloromethane: methanol = 15: 1). The product was obtained in 83.3% yield (1.15g) as a faint yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78-7.76 (m, 2H), 7.64-7.49(m, 10H), 7.34-7.23 (m, 8H), 3.60 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.86, 133.91, 132.52, 132.37, 131.74, 131.53, 131.44, 131.41, 130.73, 130.14, 129.74, 129.54, 129.47, 128.89, 126.06, 125.98, 122.60, 34.90. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{23}N_2]^+$: 387.19; found: 387.19. MS (m/z): $[M]^-$calcd for I^-: 126.91; found: 126.90.

2.3 MPI-F:

MPI-I (154.2 mg, 0.3 mmol) was dissolved in acetonitrile (18 mL). To the solution of MPI-I, a solution of AgF (50.0 mg, 0.39 mmol) in H_2O (1 mL) was added. The resulting suspension was stirred protect from light at room temperature for 1 hour, then filtered through a Buchner funnel containing kieselguhr and washed with acetonitrile. Remove the acetonitrile from the filtrate by vacuum and dissolve it again with dichloromethane (80 mL), then filtered through a Buchner funnel containing kieselguhr and washed with dichloromethane. The filtrate was evaporated by vacuum to give crude product which was suspended in isopropanol, sonicated for 10 minutes, centrifuged to remove the solvent, washed with isopropanol, centrifuged again to afford the target compound. The product was obtained in 42.1% yield (51mg) as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76-7.74 (m, 2H), 7.63-7.51 (m, 8H), 7.49-7.47 (m, 2H), 7.34-7.24 (m, 8H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.00, 133.96,

132.44, 132.32, 131.79, 131.52, 131.49, 131.44, 130.66, 130.09, 129.73, 129.52, 129.45, 128.99, 128.88, 126.11, 126.03, 122.66, 34.84. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{23}N_2]^+$: 387.19; found: 387.19.

2.4 MPI-B:

MPI-I (154.2mg, 0.3mmol) was dissolved in acetonitrile (18 mL). To the solution of MPI-I, a solution of AgBF4 (75.9 mg, 0.39 mmol) in acetonitrile (2 mL) was added. The resulting suspension was stirred protect from light at room temperature for 1 hour, then filtered through a Buchner funnel containing kieselguhr and washed with acetonitrile. Remove the acetonitrile from the filtrate by vacuum and dissolve it again with dichloromethane (25 mL), then filtered through a Buchner funnel containing kieselguhr and washed with dichloromethane. The filtrate was evaporated by vacuum to give crude product which was suspended in isopropanol, sonicated for 10 minutes, centrifuged to remove the solvent, washed with isopropanol, centrifuged again to afford the target compound. The product was obtained in 49.4% yield (70.3mg) as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70-7.67 (m, 2H), 7.60-7.54 (m, 8H), 7.44-7.42 (m, 2H), 7.35-7.20 (m, 8H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 139.91, 128.94, 128.08, 127.74, 127.05, 126.75, 126.56, 126.40, 125.32, 125.12, 124.57, 124.48, 124.36, 124.17, 123.74, 123.45, 120.96, 120.87, 117.58, 29.43. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{23}N_2]^+$: 387.19; found: 387.19. MS (m/z): $[M]^-$calcd for BF_4^-: 87.00; found: 87.00.

2.5 MPI-C:

MPI-I (154.2mg, 0.3mmol) was dissolved in acetonitrile (18 mL). To the solution of MPI-I, a solution of $AgClO_4$ (80.9 mg, 0.39 mmol) in acetonitrile (2 mL) was added. The resulting suspension was stirred protect from light at room temperature for 1 hour, then filtered through a Buchner funnel containing kieselguhr and washed with acetonitrile. Remove the acetonitrile from the filtrate by vacuum and dissolve it again with dichloromethane (25 mL), then filtered through a Buchner funnel containing kieselguhr and washed with dichloromethane. The filtrate was evaporated by vacuum

to give crude product which was suspended in isopropanol, sonicated for 10 minutes, centrifuged to remove the solvent, washed with isopropanol, centrifuged again to afford the target compound. The product was obtained in 58.3% yield (85mg) as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70-7.67 (m, 2H), 7.60-7.54 (m, 8H), 7.44-7.42 (m, 2H), 7.35-7.20 (m, 8H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.03, 133.84, 132.57, 132.37, 131.77, 131.35, 131.25, 130.77, 130.19, 129.84, 129.65, 129.56, 129.00, 128.83, 125.97, 125.88, 122.52, 34.89. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{23}N_2]^+$: 387.19; found: 387.19. MS (m/z): $[M]^-$calcd for ClO_4^-: 98.95; found: 98.95.

2.6 MPI-P:

MPI-I (102.8mg, 0.2mmol) was dissolved in acetonitrile (12 mL). To the solution of MPI-I, a solution of $AgPF_6$ (65.7 mg, 0.26 mmol) in acetonitrile (8 mL) was added. The resulting suspension was stirred protect from light at room temperature for 1 hour, then filtered through a Buchner funnel containing kieselguhr and washed with acetonitrile. Remove the acetonitrile from the filtrate by vacuum and dissolve it again with dichloromethane (15 mL), then filtered through a Buchner funnel containing kieselguhr and washed with dichloromethane. The filtrate was evaporated by vacuum to give crude product which was suspended in isopropanol, sonicated for 10 minutes, centrifuged to remove the solvent, washed with isopropanol, centrifuged again to afford the target compound. The product was obtained in 43.5% yield (46.3mg) as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.70-7.67 (m, 2H), 7.60-7.54 (m, 8H), 7.44-7.42 (m, 2H), 7.35-7.20 (m, 8H), 3.63 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 144.64, 133.54, 132.88, 132.53, 131.94, 131.37, 131.16, 131.00, 130.19, 129.97, 129.42, 129.35, 129.20, 129.00, 128.31, 125.50, 125.43, 122.11, 34.14. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{23}N_2]^+$: 387.19; found: 387.19. MS (m/z): $[M]^-$calcd for PF_6^-: 144.96; found: 144.96.

2.7 PPI:

A mixture of 9,10-Phenanthraquinone (1.04 g, 5.0 mmol), benzaldehyde (0.53 g,

5.0 mmol), aniline (2.33 g, 25.0 mmol), ammonium acetate (1.55 g, 20.0 mmol) was stirred in acetic acid (40ml) and refluxed for 3.5 h under nitrogen atmosphere. After the reaction was completed, the solvent was evaporated under reduced pressure to obtain the crude product. Purification of crude product by column chromatography (eluent: dichloromethane). The product was obtained in 85.9% yield (1.59 g) as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (d, J = 8.4 Hz, 1H), 8.87 (d, J = 8.0 Hz, 1H), 8.70 (dd, J1 = 8.0 Hz, J2 = 1.2 Hz, 1H), 7.78 (t, J = 6.8 Hz, 1H), 7.72 - 7.65 (m, 6H), 7.59- 7.53 (m, 3H), 7.38-7.31 (m, 4H), 7.08 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.05, 138.65, 136.94, 130.79, 130.74, 130.68, 129.64, 129.61, 129.46, 128.98, 128.67, 128.24, 128.16, 127.94, 127.20, 127.10, 126.22, 125.68, 124.98, 124.15, 122.97, 122.50, 120.66. MS (m/z): $[M+H]^+$ calcd for $[C_{27}H_{19}N_2]^+$: 371.15; found: 371.15.

2.8 MPPI-I:

A mixture of PPI (1.50 g, 4.05 mmol), Methyl iodide (5.75 g, 40.5 mmol), acetonitrile (90 mL) was stirred for 72h at 70°C. After the reaction is completed, slowly cool the reaction solution to room temperature. Filter the reaction solution to obtain a filter cake, and wash the filter cake with acetonitrile three times to get the target compound. The product was obtained in 73.6% yield (1.53 g) as a faint yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.21-9.18 (m, 1H), 9.14 (d, J = 8.4 Hz, 1H), 8.92-8.89 (m, 1H), 8.03-7.96 (m, 2H), 7.82-7.77 (m, 5H), 7.70-7.56 (m, 6H), 7.51 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 4.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.83, 135.46, 132.88, 132.11, 131,79, 131.02, 130.08, 129.89, 129.48, 129.34, 128.94, 128.79, 128.68, 128.63, 126.76, 126.28, 125.49, 125.46, 123.14, 122.05, 121.38, 121.22, 120.44, 38.28. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{21}N_2]^+$: 385.17; found: 385.17. MS (m/z): $[M]^-$calcd for I^-: 126.91; found: 126.90.

2.9 MPPI-F:

MPPI-I (153.6 mg, 0.3 mmol) was dissolved in acetonitrile (160 mL). To the solution of MPPI-I, a solution of AgF (50.0 mg, 0.39 mmol) in H_2O (1 mL) was added.

The resulting suspension was stirred protect from light at room temperature for 1 hour, then filtered through a Buchner funnel containing kieselguhr and washed with acetonitrile. Remove the acetonitrile from the filtrate by vacuum and dissolve it again with dichloromethane (80 mL), then filtered through a Buchner funnel containing kieselguhr and washed with dichloromethane. The filtrate was evaporated by vacuum to give crude product which was suspended in isopropanol, sonicated for 10 minutes, centrifuged to remove the solvent, washed with isopropanol, centrifuged again to afford the target compound. The product was obtained in 35.5% yield (43 mg) as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20-9.18 (m, 1H), 9.13 (d, J = 8.4 Hz, 1H), 8.93-8.90 (m, 1H), 8.02-7.96 (m, 2H), 7.82-7.77 (m, 5H), 7.72-7.56 (m, 6H), 7.51 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 4.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.87, 135.45, 132.89, 132.11, 131.73, 131.03, 130.08, 129.88, 129.50, 129.35, 128.93, 128.80, 128.69, 128.64, 126.74, 126.26, 125.49, 125.45, 123.14, 122.04, 121.38, 121.20, 120.42, 38.21. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{21}N_2]^+$: 385.17; found: 385.17.

2.10 MPPI-B:

MPPI-I (230.4 mg, 0.45 mmol) was dissolved in acetonitrile (100 mL). To the solution of MPPI-I, a solution of $AgBF_4$ (113.85 mg, 0.585 mmol) in acetonitrile (2 mL) was added. The resulting suspension was stirred protect from light at room temperature for 1 hour, then filtered through a Buchner funnel containing kieselguhr and washed with acetonitrile. Remove the acetonitrile from the filtrate by vacuum and dissolve it again with dichloromethane (100 mL), then filtered through a Buchner funnel containing kieselguhr and washed with dichloromethane. The filtrate was evaporated by vacuum to give crude product which was suspended in isopropanol, sonicated for 10 minutes, centrifuged to remove the solvent, washed with isopropanol, centrifuged again to afford the target compound. The product was obtained in 68.3% yield (145 mg) as a faint yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.21-9.18 (m, 1H), 9.13 (d, J = 8.4 Hz, 1H), 8.92-8.90 (m, 1H), 8.02-7.96 (m, 2H), 7.82-7.77 (m, 5H), 7.70-7.57 (m, 6H), 7.51 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 4.38 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6) δ 149.87, 135.45, 132.89, 132.11, 131.72, 131.03, 130.07, 129.88, 129.51, 129.36, 128.92, 128.81, 128.70, 128.65, 126.75, 126.25, 125.49, 125.46, 123.13, 122.04, 121.38, 121.19, 120.42, 38.20. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{21}N_2]^+$: 385.17; found: 385.17. MS (m/z): $[M]^-$calcd for BF_4^-: 87.00; found: 87.00.

2.11 MPPI-C:

MPPI-I (230.4 mg, 0.45 mmol) was dissolved in acetonitrile (100 mL). To the solution of MPPI-I, a solution of $AgClO_4$ (121.35 mg, 0.585 mmol) in acetonitrile (2 mL) was added. The resulting suspension was stirred protect from light at room temperature for 1 hour, then filtered through a Buchner funnel containing kieselguhr and washed with acetonitrile. Remove the acetonitrile from the filtrate by vacuum and dissolve it again with dichloromethane (100 mL), then filtered through a Buchner funnel containing kieselguhr and washed with dichloromethane. The filtrate was evaporated by vacuum to give crude product which was suspended in isopropanol, sonicated for 10 minutes, centrifuged to remove the solvent, washed with isopropanol, centrifuged again to afford the target compound. The product was obtained in 40.4% yield (88 mg) as a faint yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20-9.18 (m, 1H), 9.13 (d, J = 8.4 Hz, 1H), 8.93-8.90 (m, 1H), 8.02-7.96 (m, 2H), 7.82-7.77 (m, 5H), 7.70-7.56 (m, 6H), 7.51 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 7.6 Hz, 1H), 4.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.86, 135.45, 132.89, 132.11, 131.73, 131.03, 130.08, 129.88, 129.51, 129.35, 128.93, 128.80, 128.69, 128.64, 126.75, 126.26, 125.48, 125.45, 123.13, 122.04, 121.38, 121.20, 120.42, 38.21. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{21}N_2]^+$: 385.17; found: 385.17. MS (m/z): $[M]^-$calcd for ClO_4^-: 98.95; found: 98.95.

2.12 MPPI-P:

MPPI-I (230.4 mg, 0.45 mmol) was dissolved in acetonitrile (100 mL). To the solution of MPPI-I, a solution of $AgPF_6$ (147.83 mg, 0.585 mmol) in acetonitrile (20 mL) was added. The resulting suspension was stirred protect from light at room

temperature for 1 hour, then filtered through a Buchner funnel containing kieselguhr and washed with acetonitrile. Remove the acetonitrile from the filtrate by vacuum and dissolve it again with dichloromethane (100 mL), then filtered through a Buchner funnel containing kieselguhr and washed with dichloromethane. The filtrate was evaporated by vacuum to give crude product which was suspended in isopropanol, sonicated for 10 minutes, centrifuged to remove the solvent, washed with isopropanol, centrifuged again to afford the target compound. The product was obtained in 62.9% yield (150 mg) as a faint yellow powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.21-9.17 (m, 1H), 9.14 (d, J = 8.4 Hz, 1H), 8.92-8.90 (m, 1H), 8.02-7.96 (m, 2H), 7.82-7.77 (m, 5H), 7.71-7.57 (m, 6H), 7.51 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 4.38 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.87, 135.45, 132.89, 132.11, 131.72, 131.03, 130.07, 129.88, 129.50, 129.35, 128.93, 128.81, 128.69, 128.65, 126.75, 126.25, 125.49, 125.46, 123.13, 122.04, 121.38, 121.19, 120.42, 38.20. MS (m/z): $[M]^+$ calcd for $[C_{28}H_{21}N_2]^+$: 385.17; found: 385.17. MS (m/z): $[M]^-$calcd for PF_6^-: 144.96; found: 144.96.

2.13 detection process of $ADPNa_2$ and its derivatives

The initial solution of MPPI-B (10^{-3} mol/L or 10^{-4} mol/L) was prepared in DMSO. Different proteins and biological small molecules solution were prepared in H_2O, respectively. Fluorescence emission spectra of MPPI-B for the detection of various compounds were measured in 1/99 (v/v) DMSO/PBS mixture (MPPI-B: 10^{-5} mol/L or 10^{-6} mol/L). The detailed measurement methods were conducted as followed:

Method (using $ADPNa_2$ as an example): 10 μL MPPI-B (10^{-4} mol/L, in DMSO) and 990 μL PBS were first mixed to obtain the MPPI-B solution with the concentration of 10^{-6} mol/L in a 1/99 (v/v) DMSO/PBS mixture. The different volumes of $ADPNa_2$ initial aqueous solution (1 mg/mL) were added into MPPI-B solution to form the solution of MPPI-B (10^{-6} mol/L) and different $ADPNa_2$ concentration (2-12 ug/mL) in a 1/99 (v/v) DMSO/PBS mixture.

3. ^{1}H, ^{13}C NMR and MS spectra

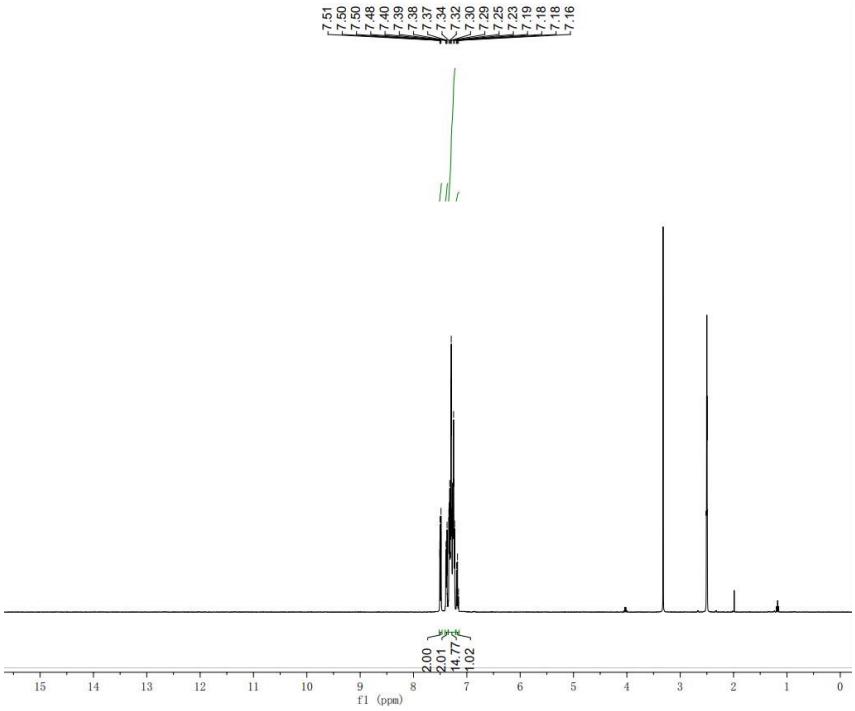


Figure S1. ^{1}H-NMR spectrum of PI. Solvent: DMSO-d_6.

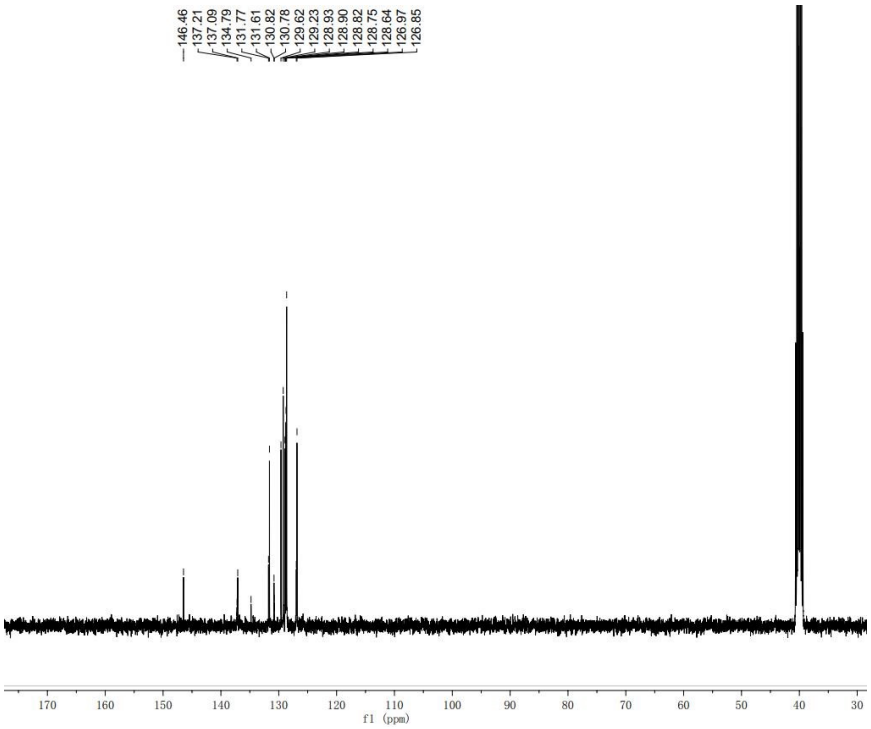


Figure S2. ^{13}C-NMR spectrum of PI. Solvent: DMSO-d_6.

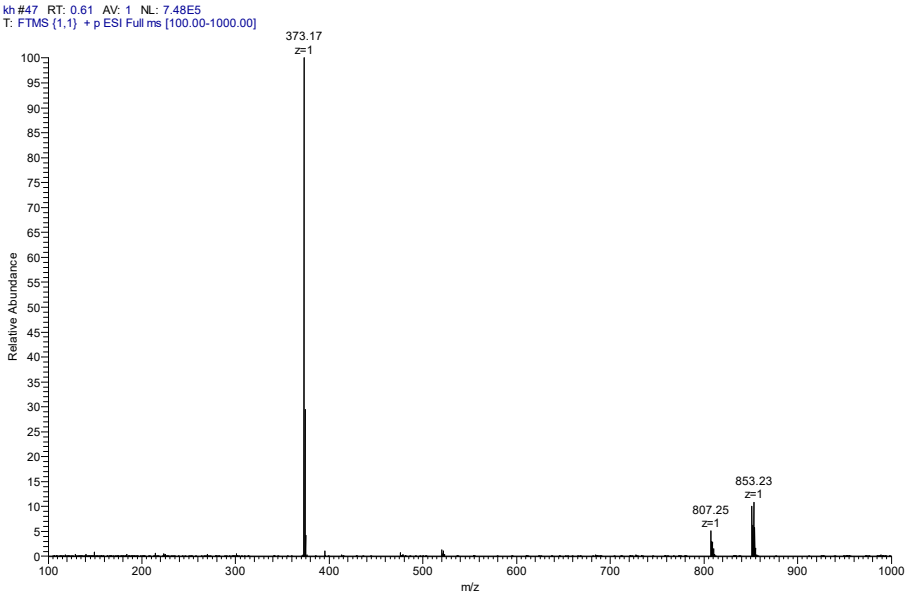


Figure S3. MS spectrum of PI.

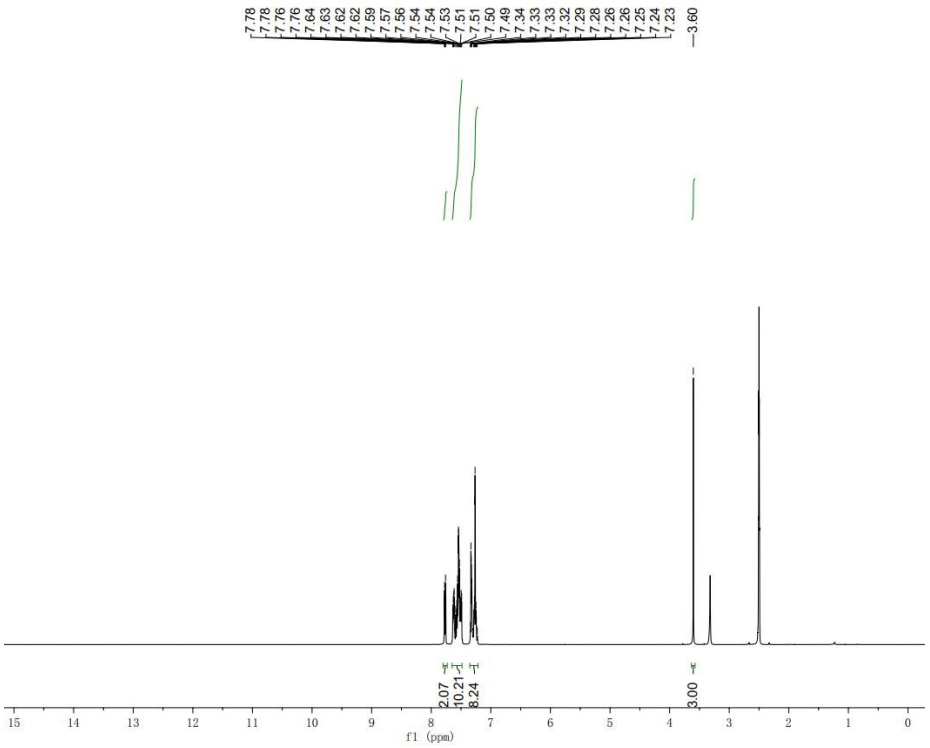


Figure S4. ^{1}H-NMR spectrum of MPI-I. Solvent: DMSO-d_6.

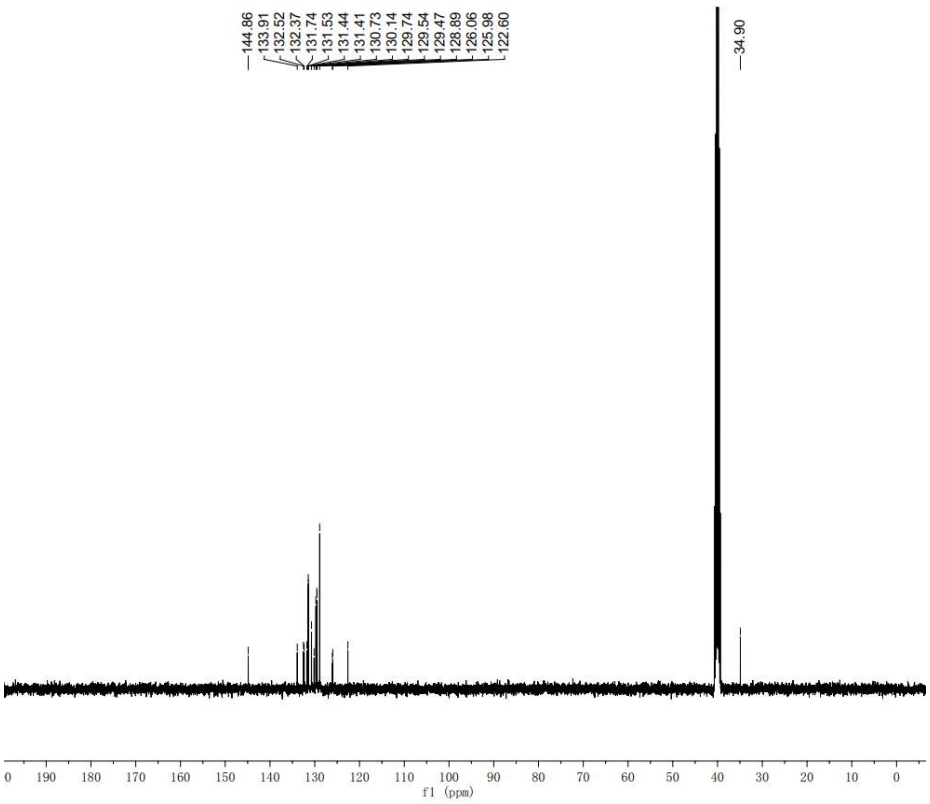


Figure S5. ^{13}C-NMR spectrum of MPI-I. Solvent: DMSO-d_6.

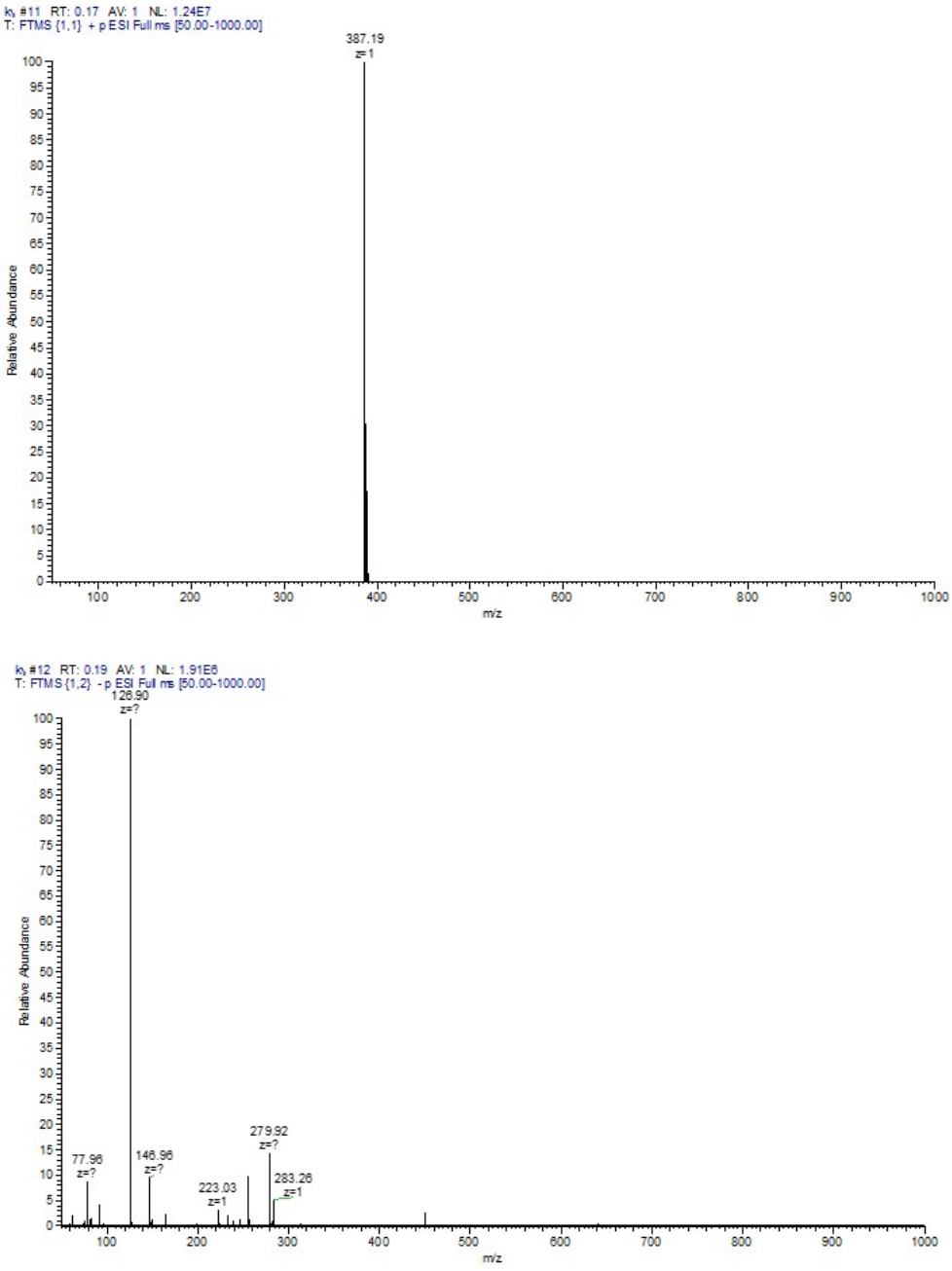


Figure S6. MS spectrum of MPI-I.

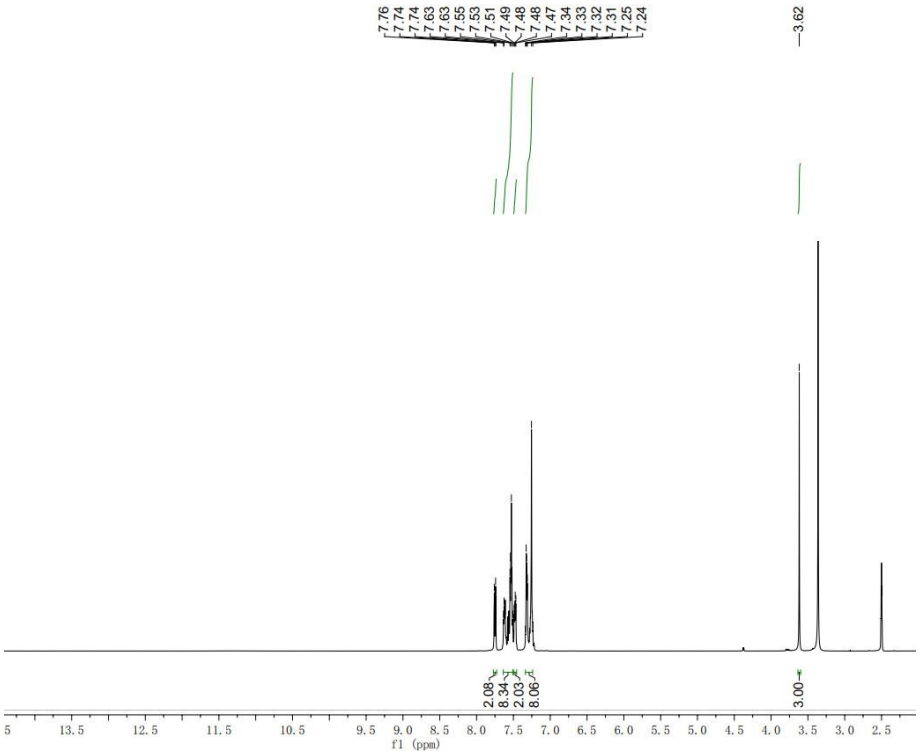


Figure S7. ^{1}H-NMR spectrum of MPI-F. Solvent: DMSO-d_6.

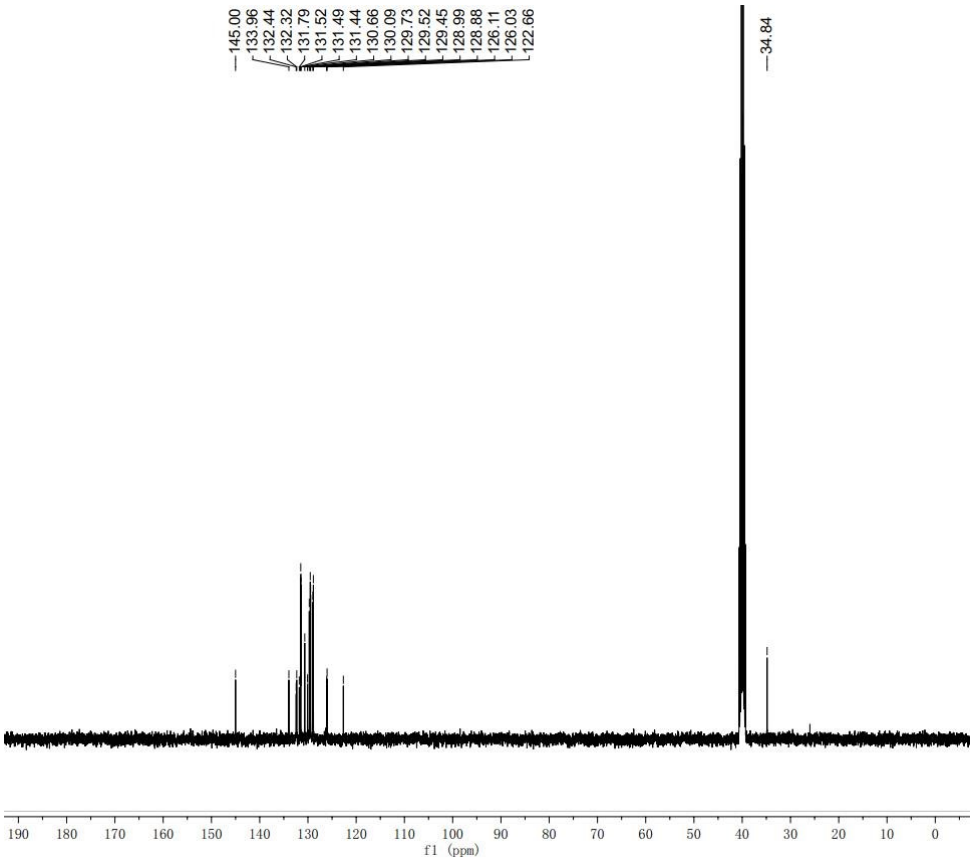


Figure S8. ^{13}C-NMR spectrum of MPI-F. Solvent: DMSO-d_6.

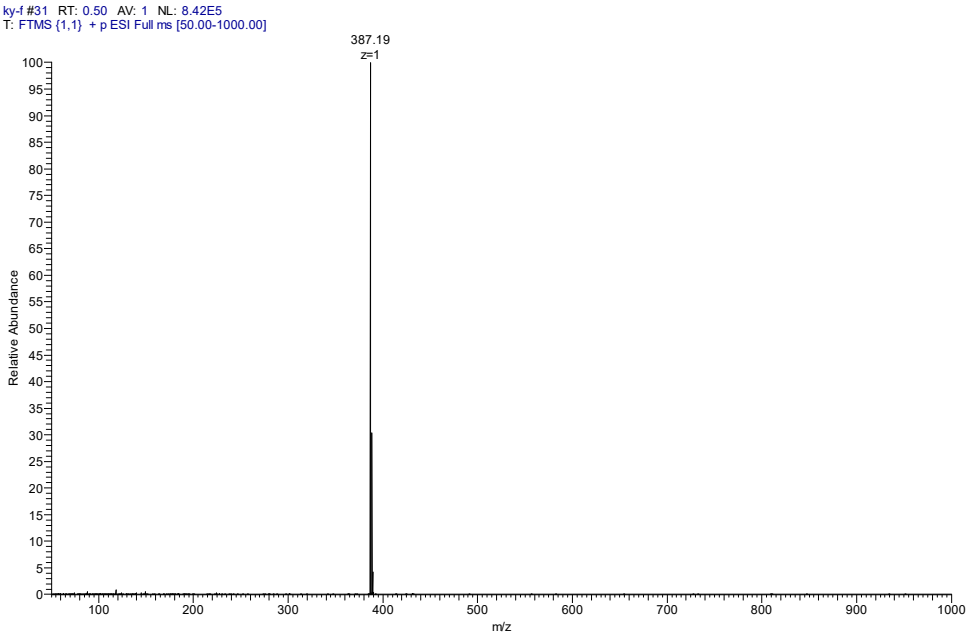


Figure S9. MS spectrum of MPI-F.

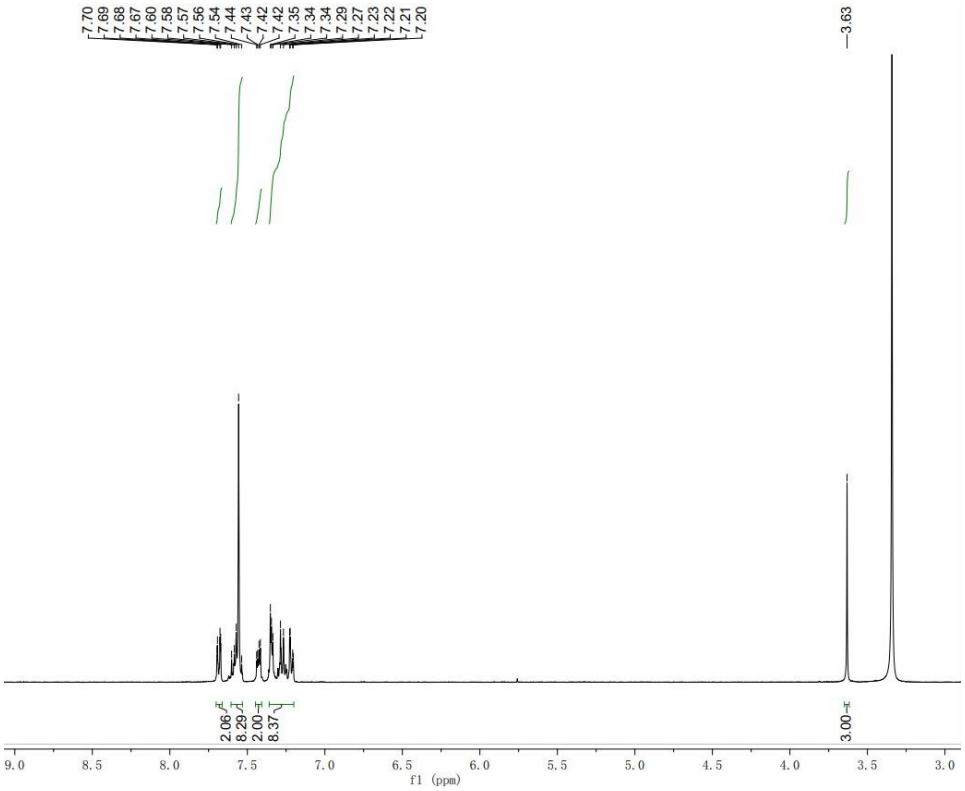


Figure S10. ^{1}H-NMR spectrum of MPI-B. Solvent: DMSO-d_6.

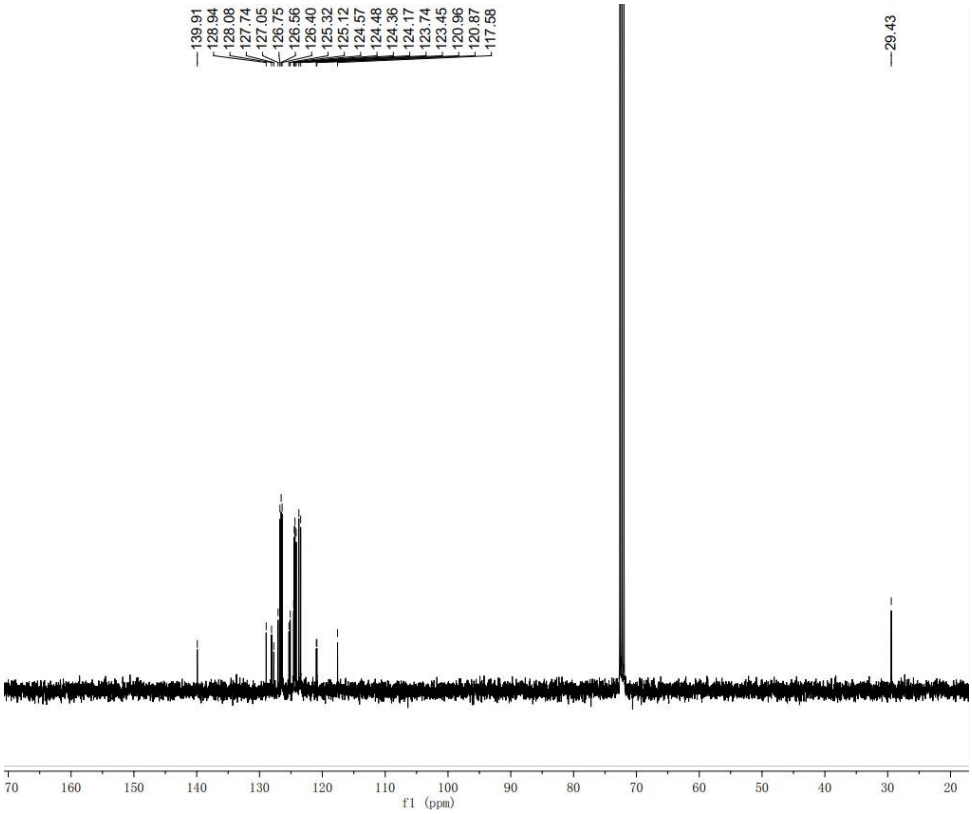


Figure S11. ^{13}C-NMR spectrum of MPI-B. Solvent: DMSO-d_6.

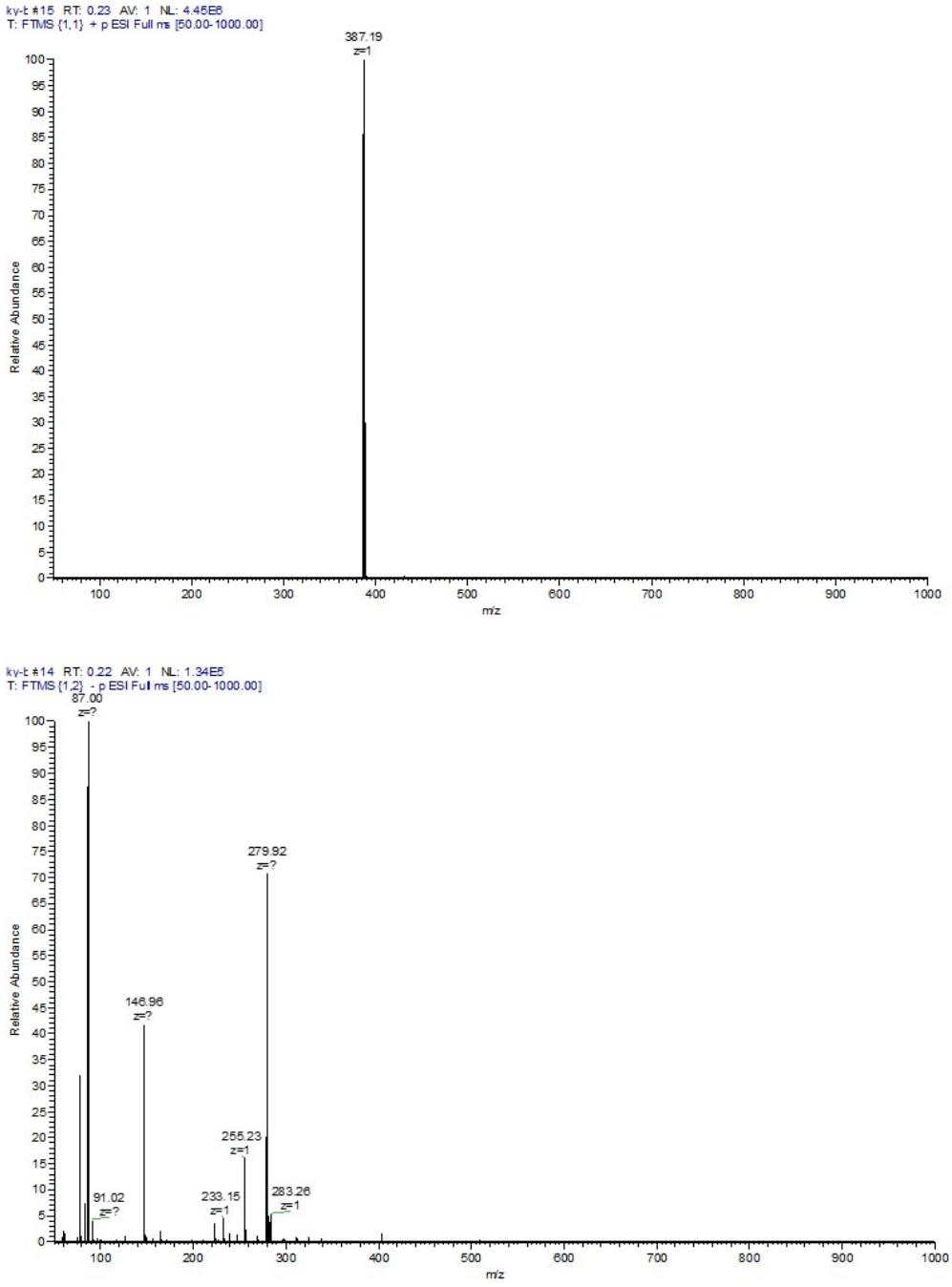


Figure S12. MS spectrum of MPI-B.

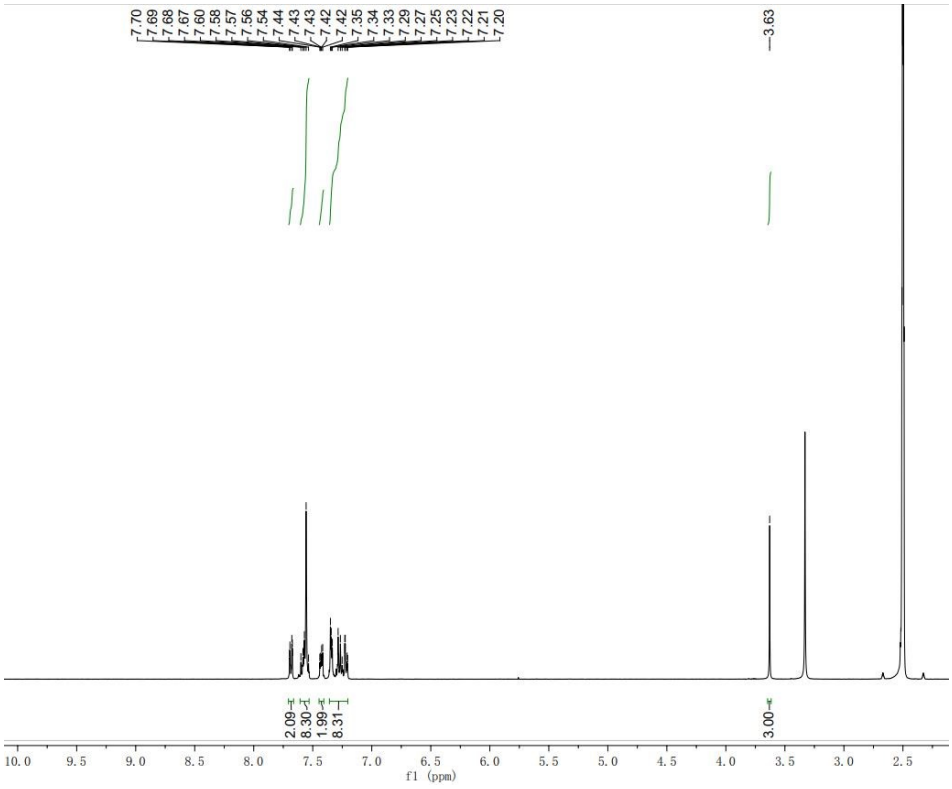


Figure S13. ^{1}H-NMR spectrum of MPI-C. Solvent: DMSO-d_6.

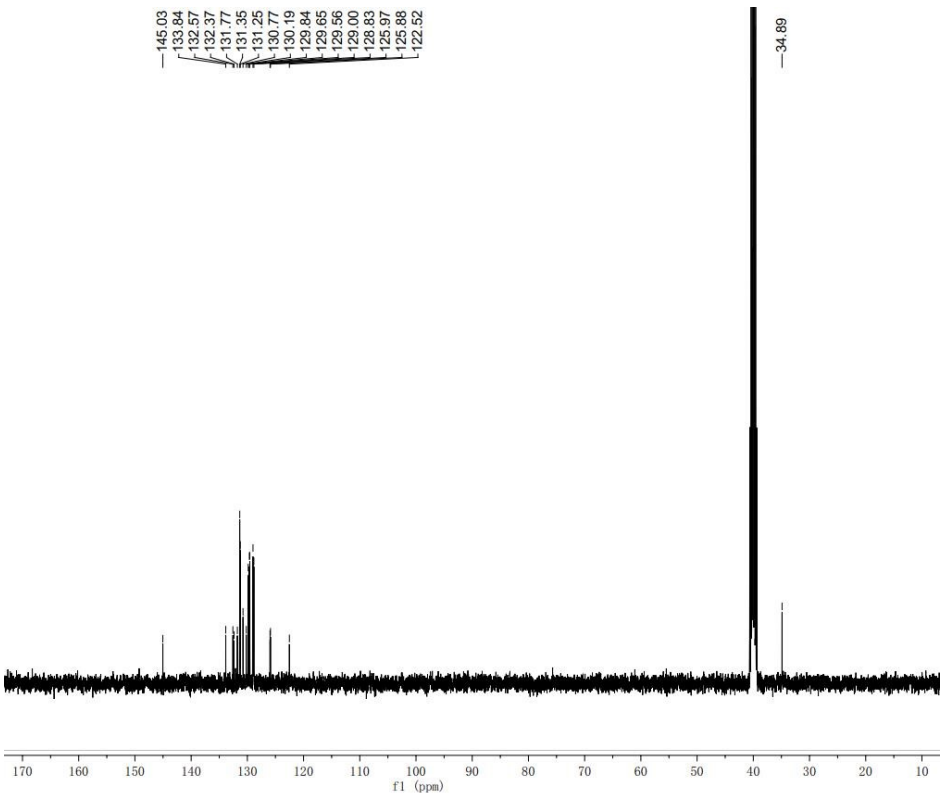


Figure S14. ^{13}C-NMR spectrum of MPI-C. Solvent: DMSO-d_6.

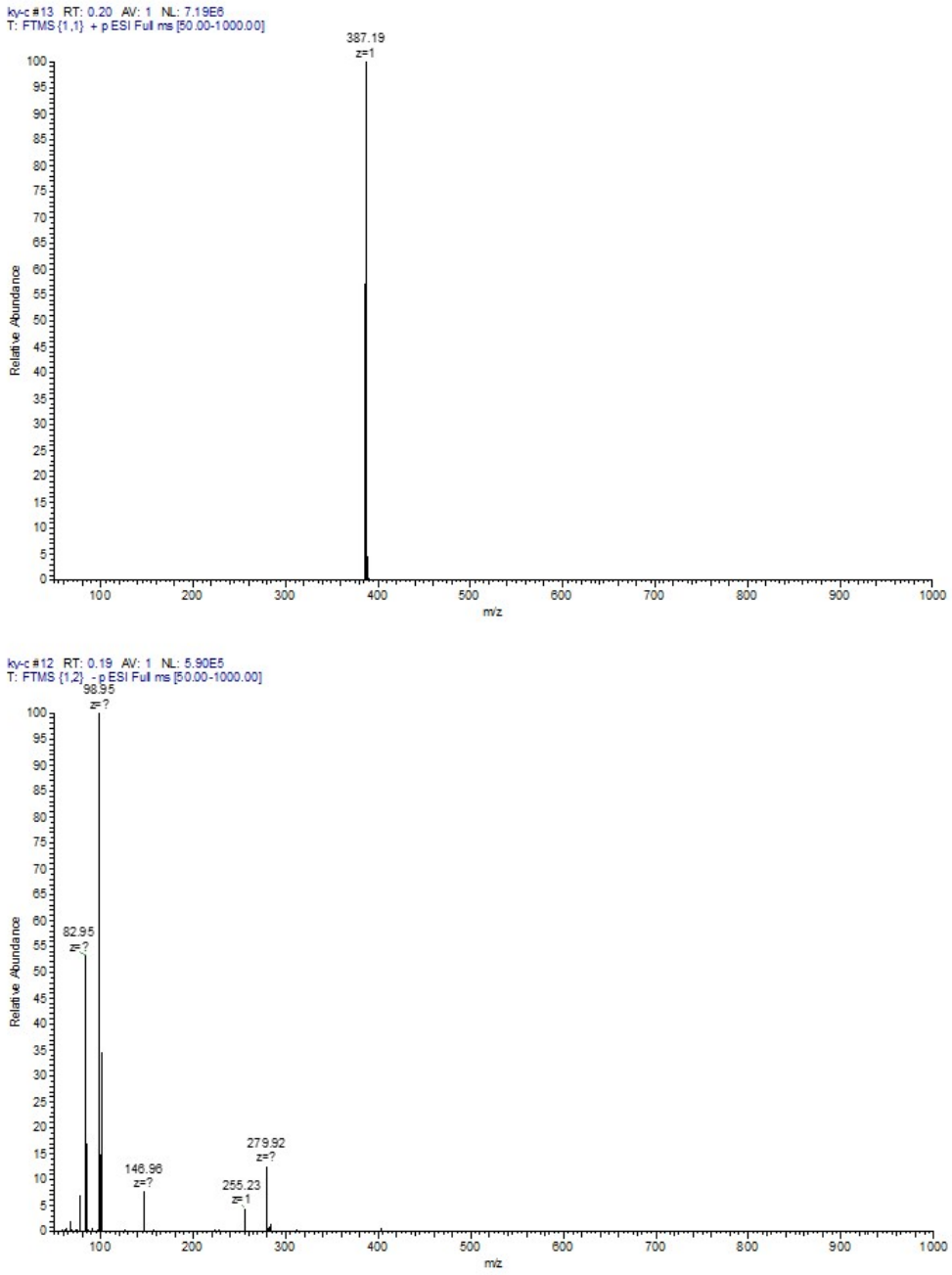


Figure S15. MS spectrum of MPI-C.

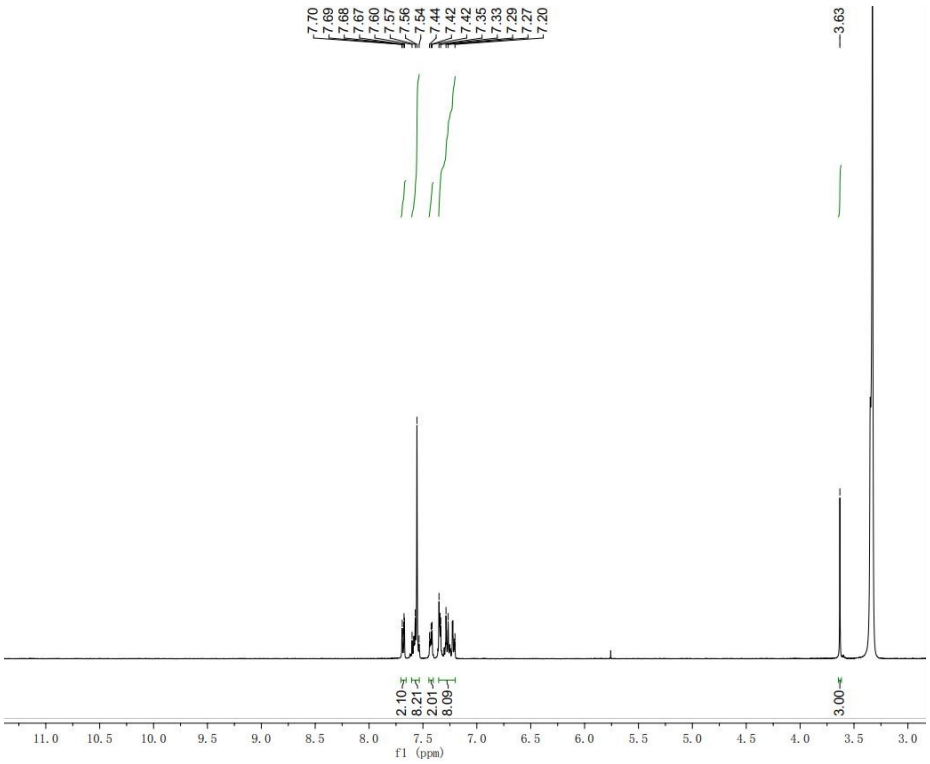


Figure S16. ^{1}H-NMR spectrum of MPI-P. Solvent: DMSO-d_6.

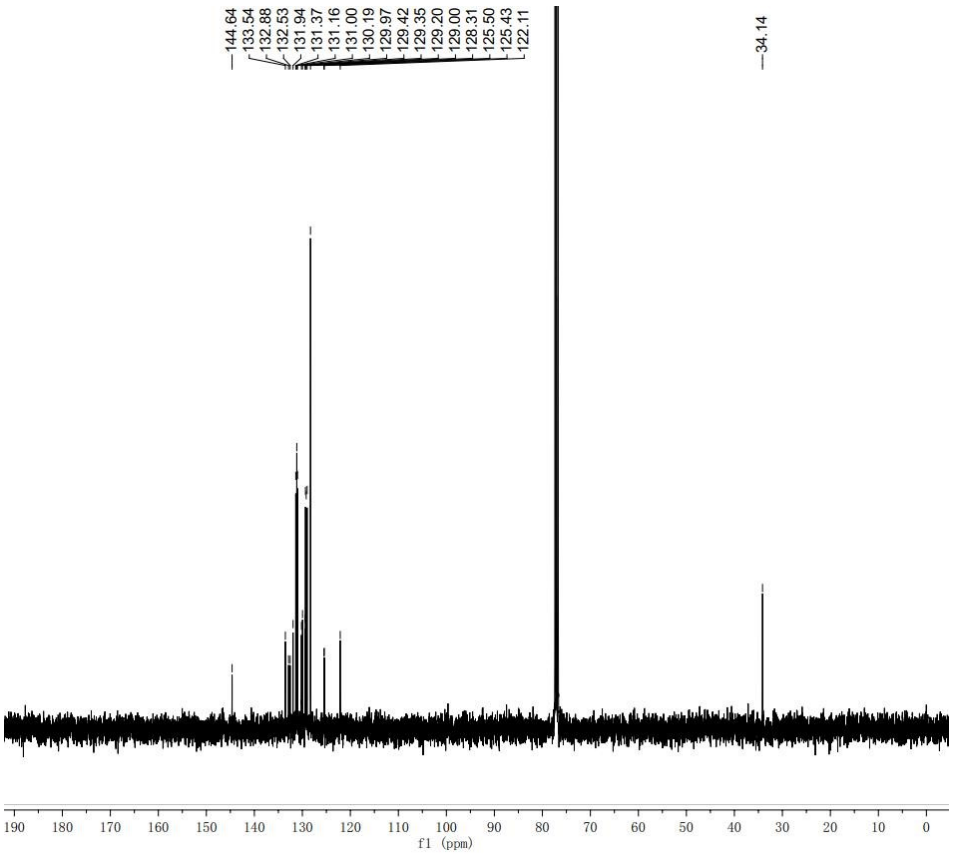


Figure S17. ^{13}C-NMR spectrum of MPI-P. Solvent: DMSO-d_6.

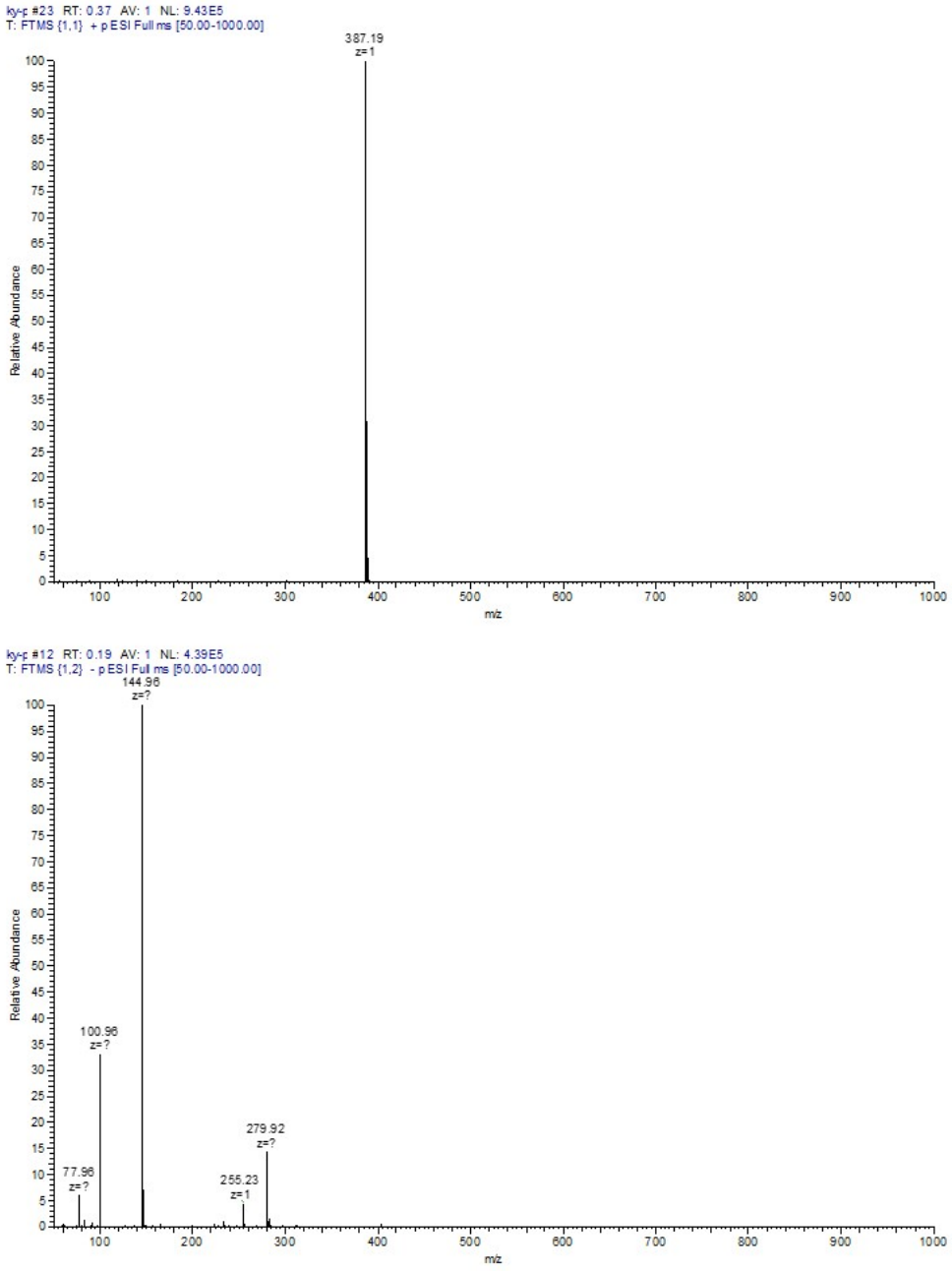


Figure S18. MS spectrum of MPI-P.

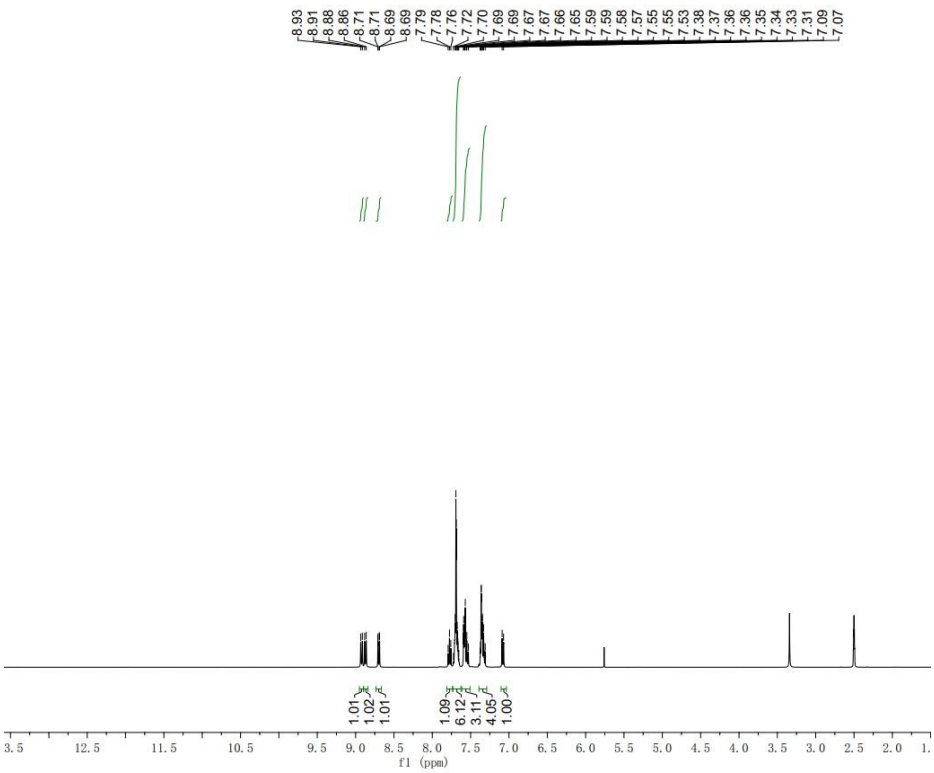


Figure S19. ^{1}H-NMR spectrum of PPI. Solvent: DMSO-d_6.

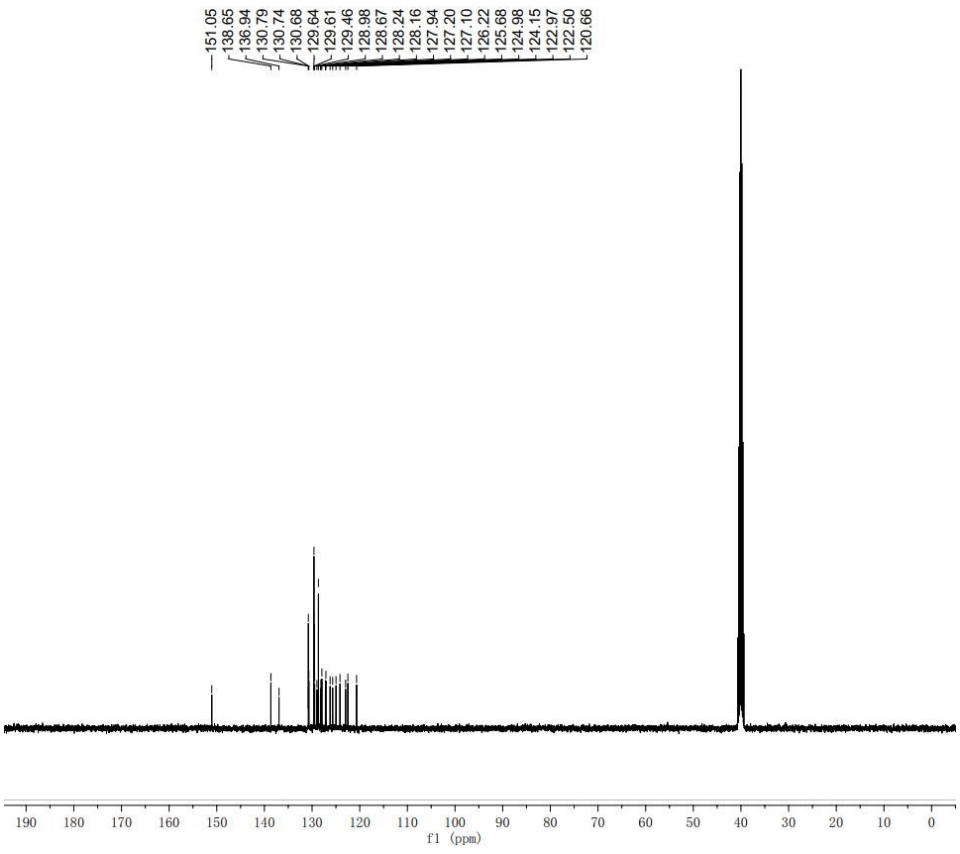


Figure S20. ^{13}C-NMR spectrum of PPI. Solvent: DMSO-d_6.

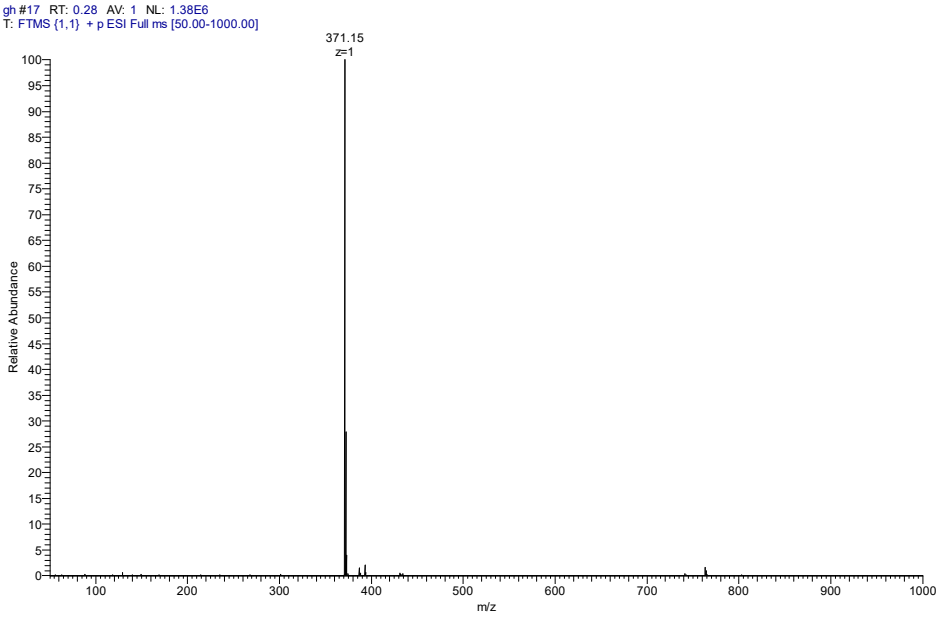


Figure S21. MS spectrum of PPI.

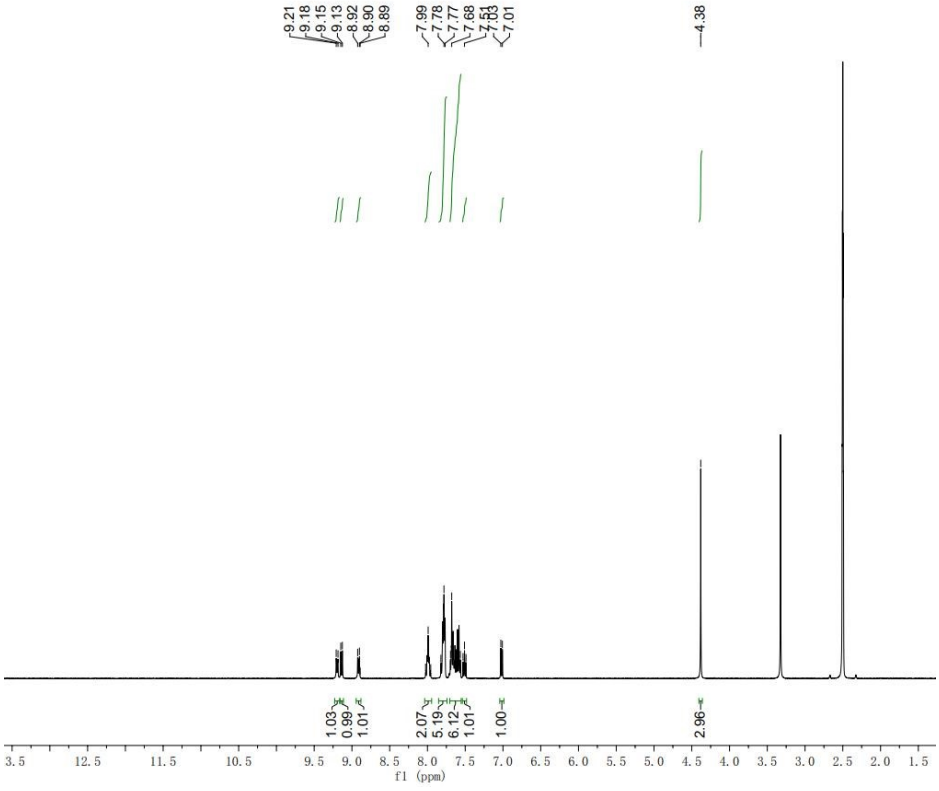


Figure S22. ^{1}H-NMR spectrum of MPPI-I. Solvent: DMSO-d_6.

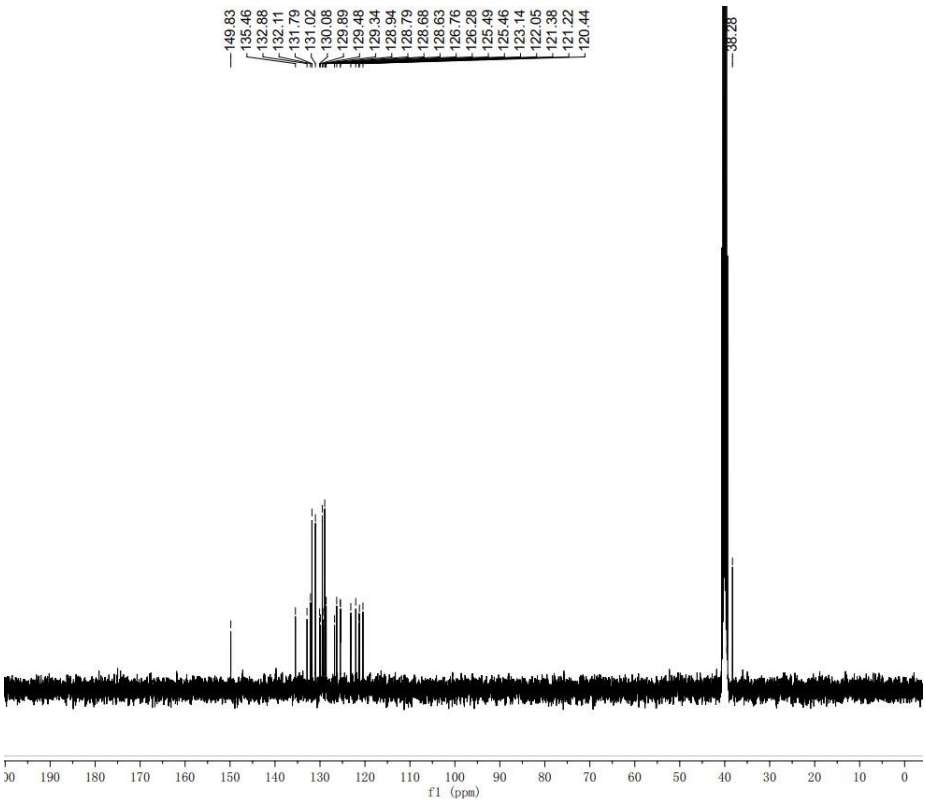


Figure S23. ^{13}C-NMR spectrum of MPPI-I. Solvent: DMSO-d_6.

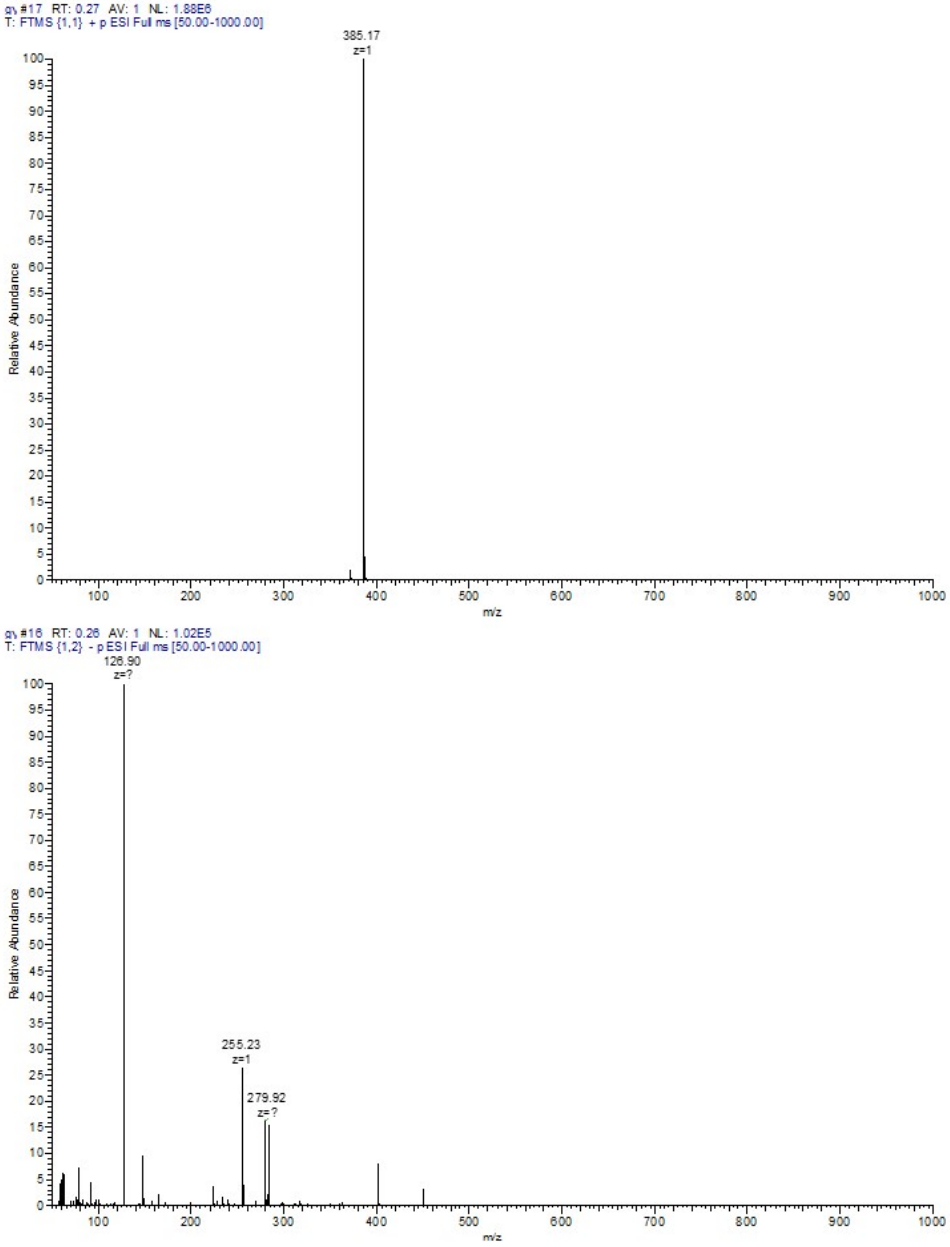


Figure S24. MS spectrum of MPPI-I.

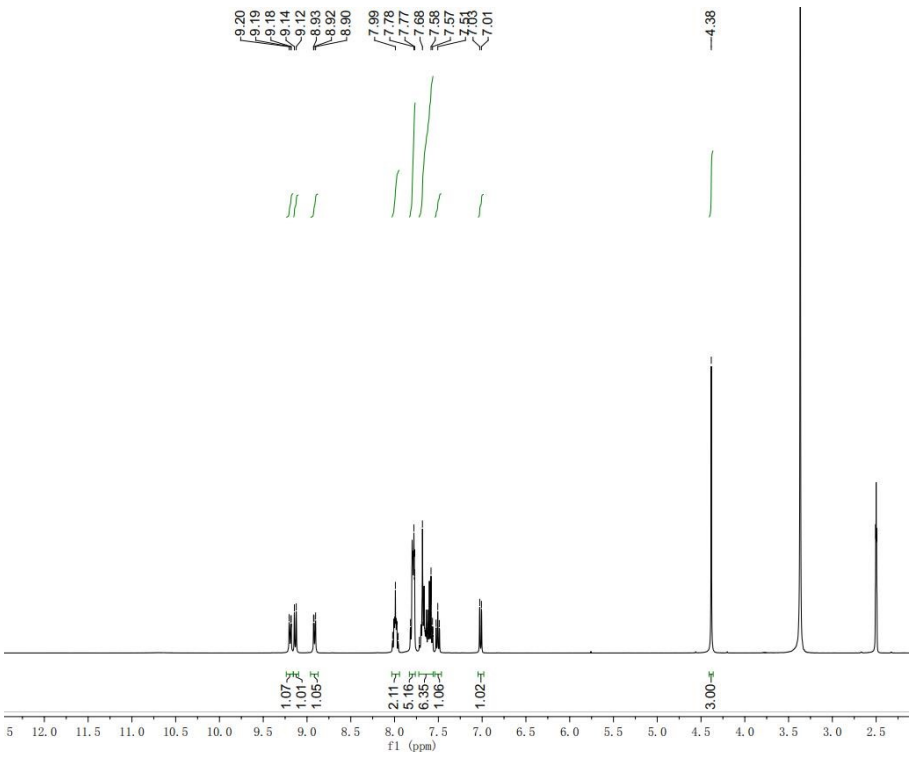


Figure S25. ^{1}H-NMR spectrum of MPPI-F. Solvent: DMSO-d_6.

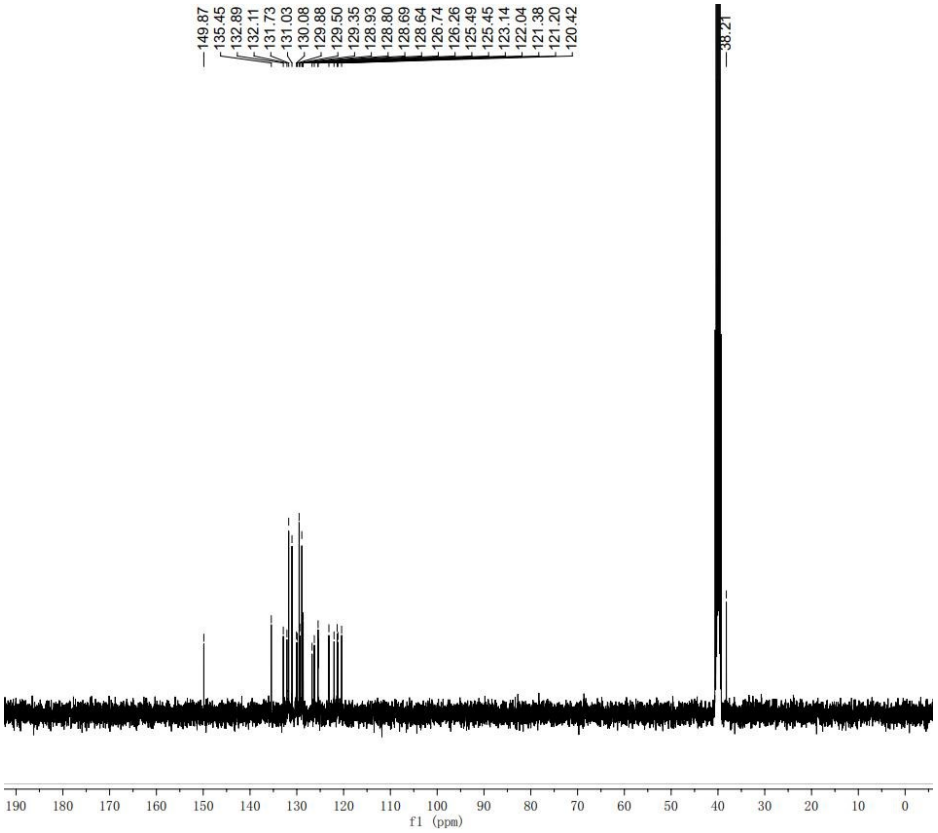


Figure S26. ^{13}C-NMR spectrum of MPPI-F. Solvent: DMSO-d_6.

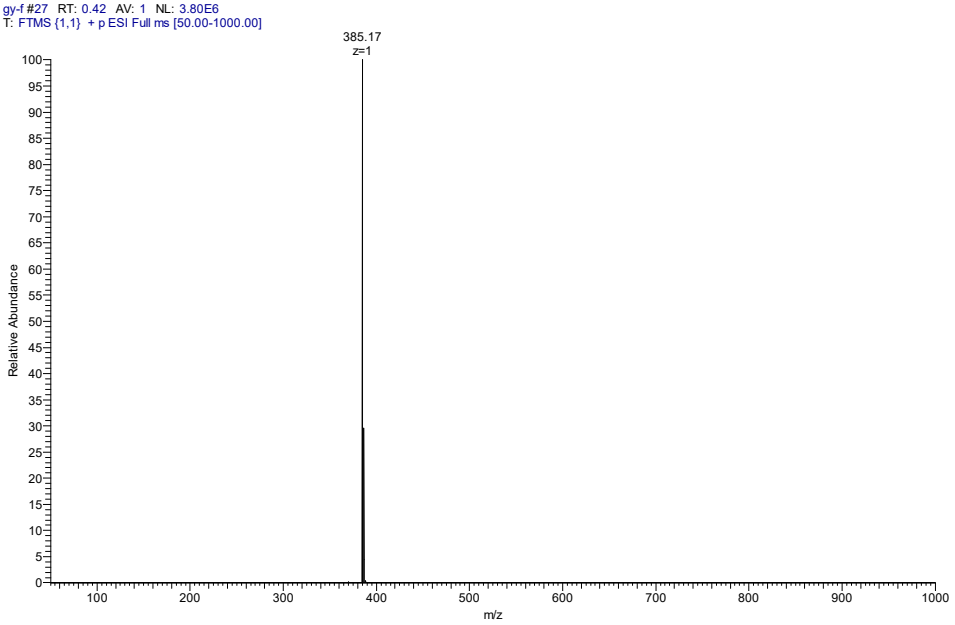


Figure S27. MS spectrum of MPPI-F.

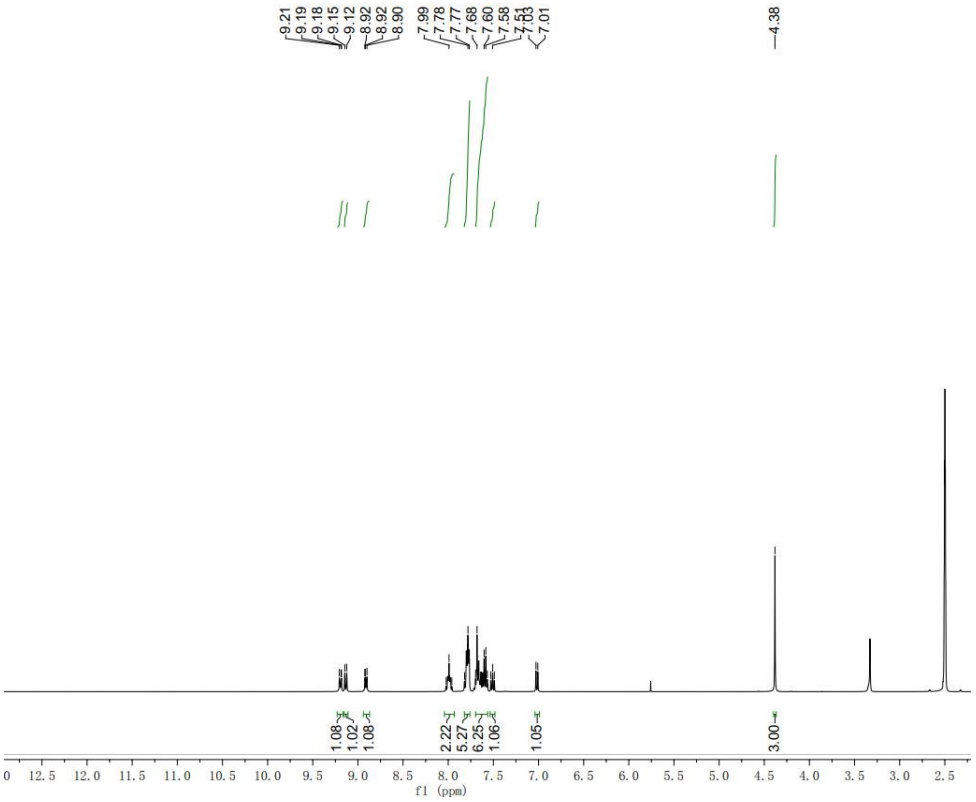


Figure S28. ^{1}H-NMR spectrum of MPPI-B. Solvent: DMSO-d_6.

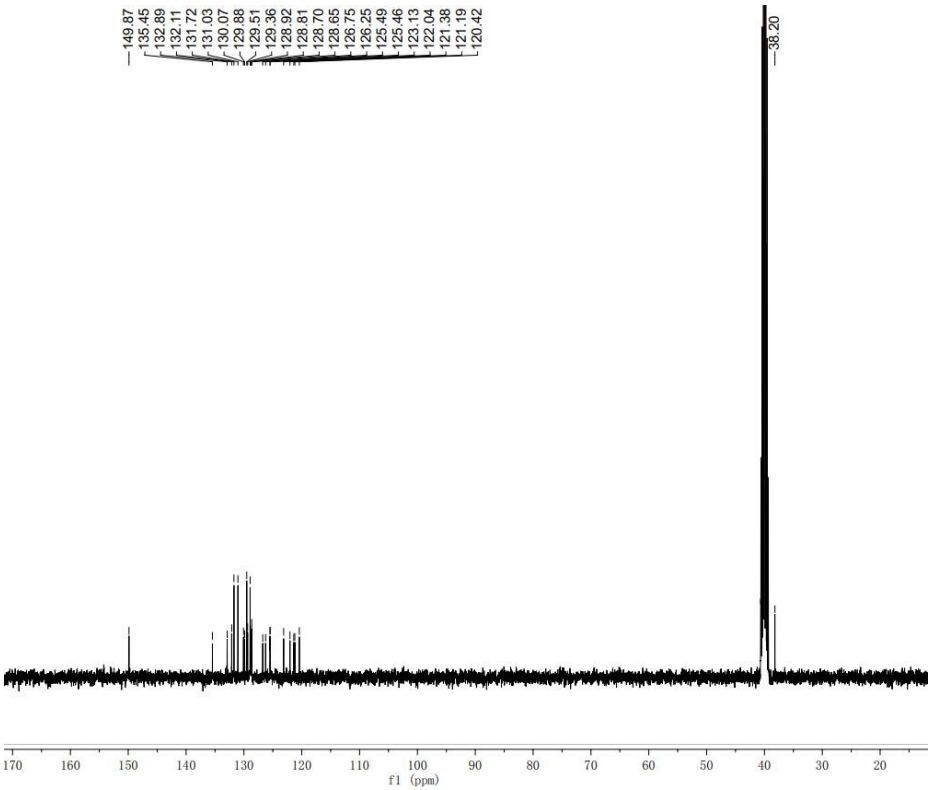


Figure S29. ^{13}C-NMR spectrum of MPPI-B. Solvent: DMSO-d_6.

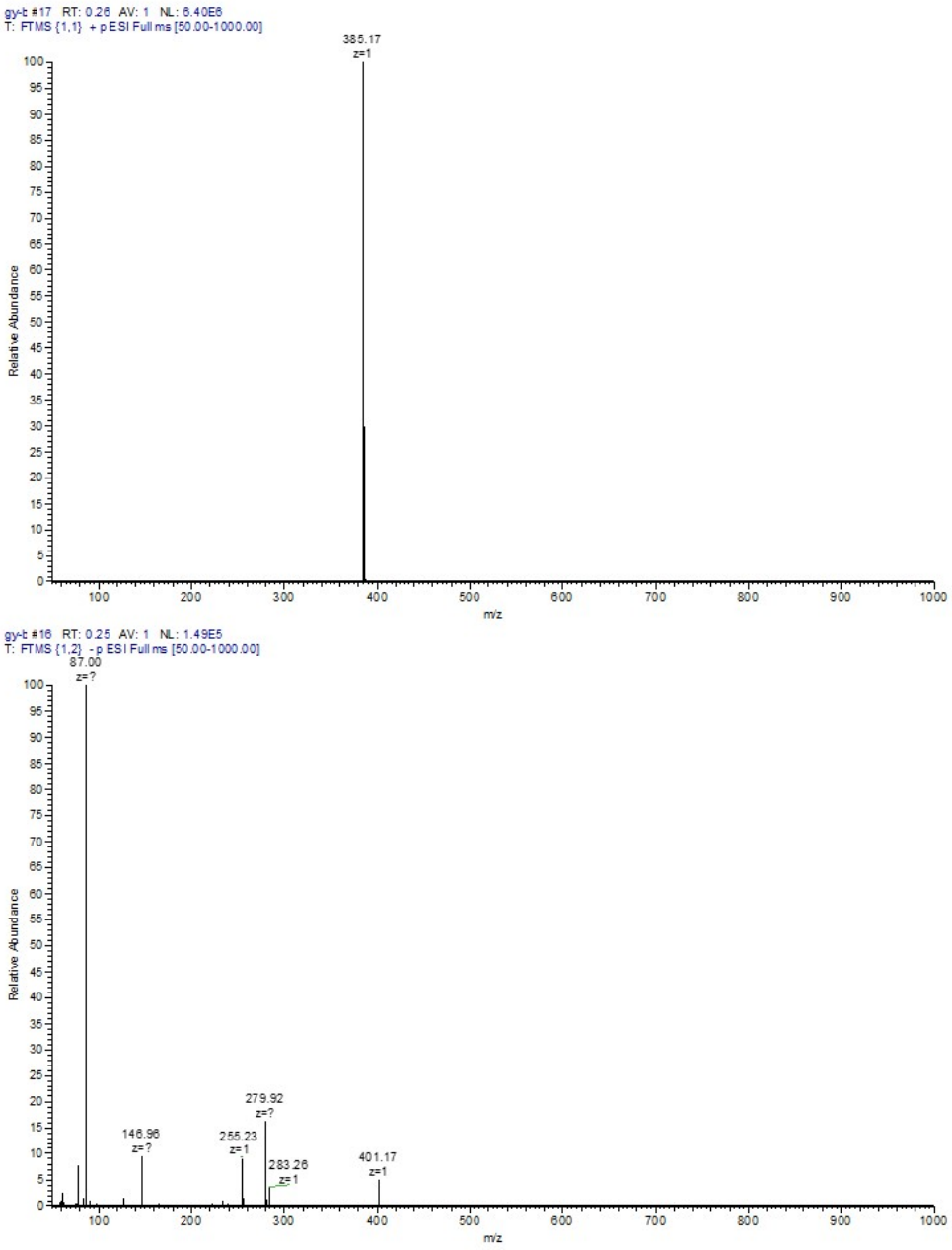


Figure S30. MS spectrum of MPPI-B.

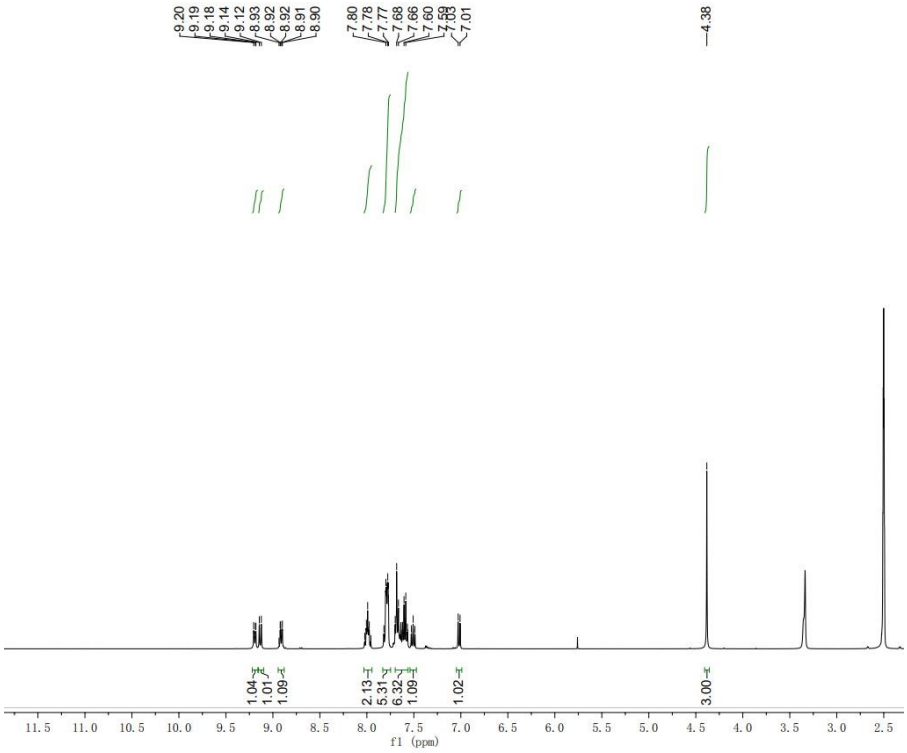


Figure S31. ^{1}H-NMR spectrum of MPPI-C. Solvent: DMSO-d_6.

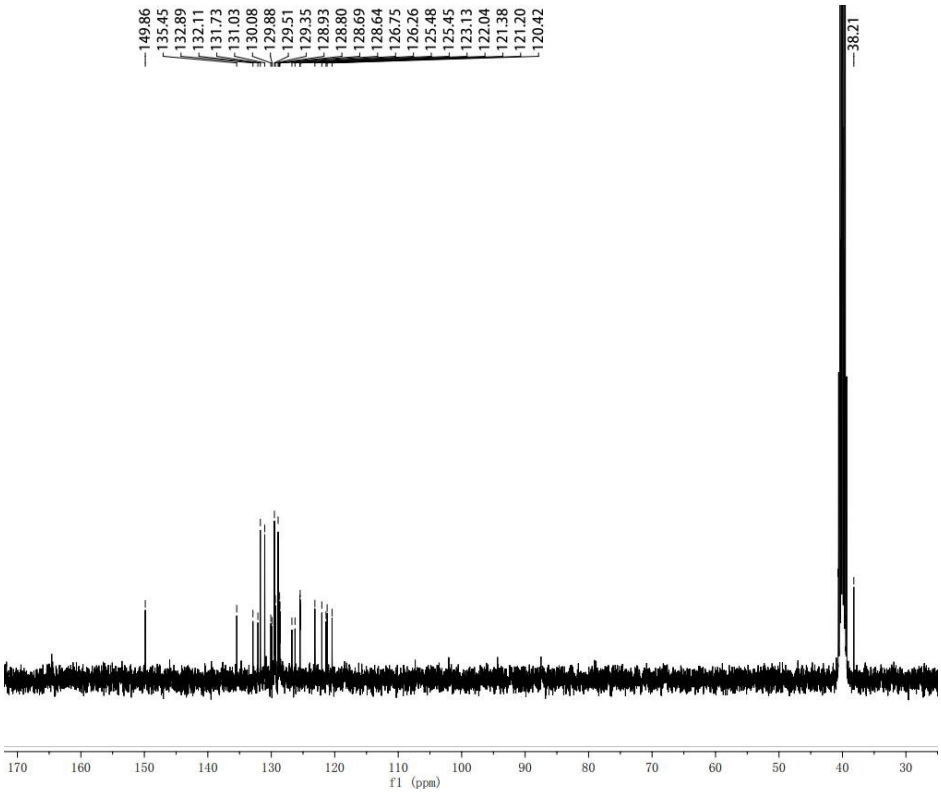


Figure S32. ^{13}C-NMR spectrum of MPPI-C. Solvent: DMSO-d_6.

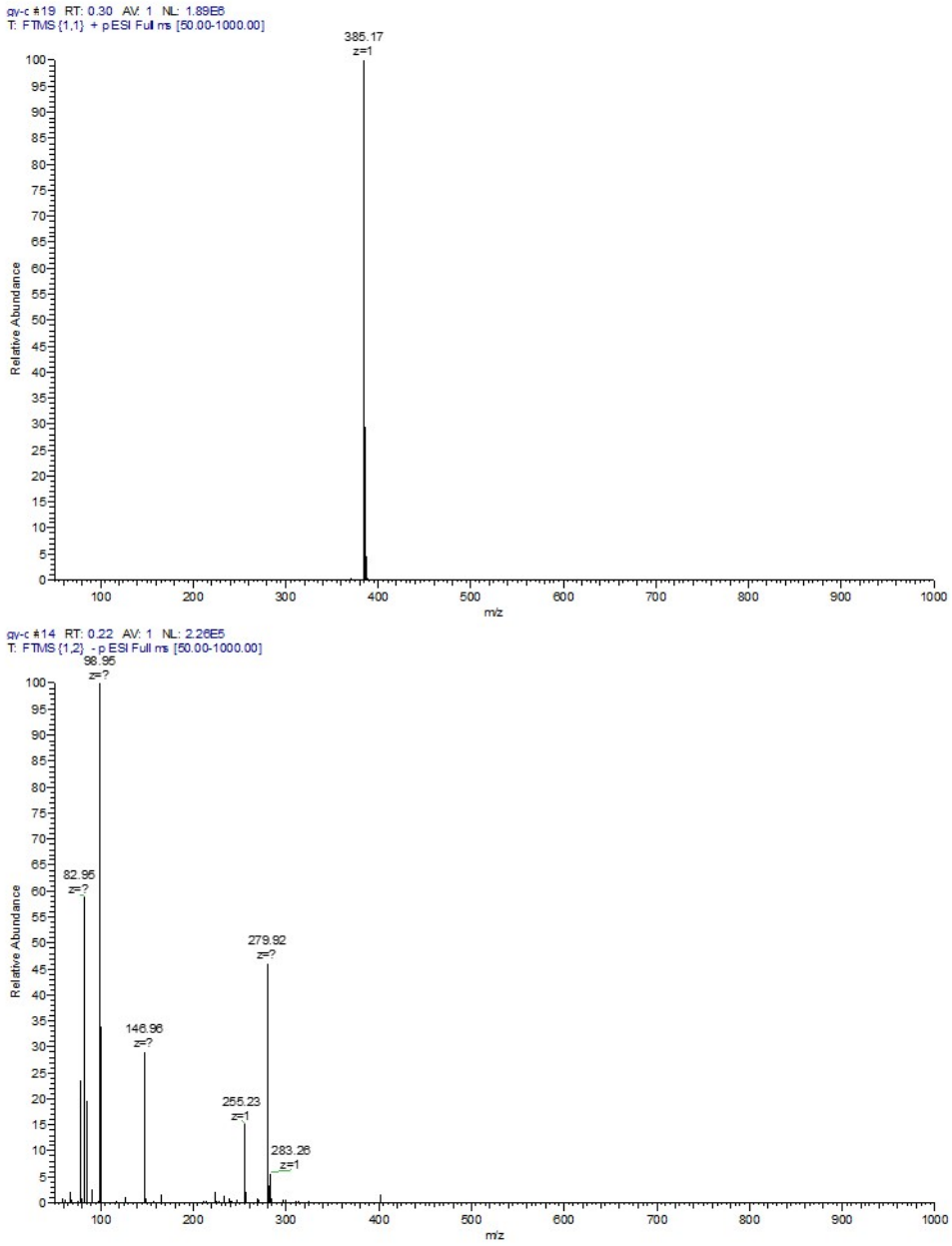


Figure S33. MS spectrum of MPPI-C.

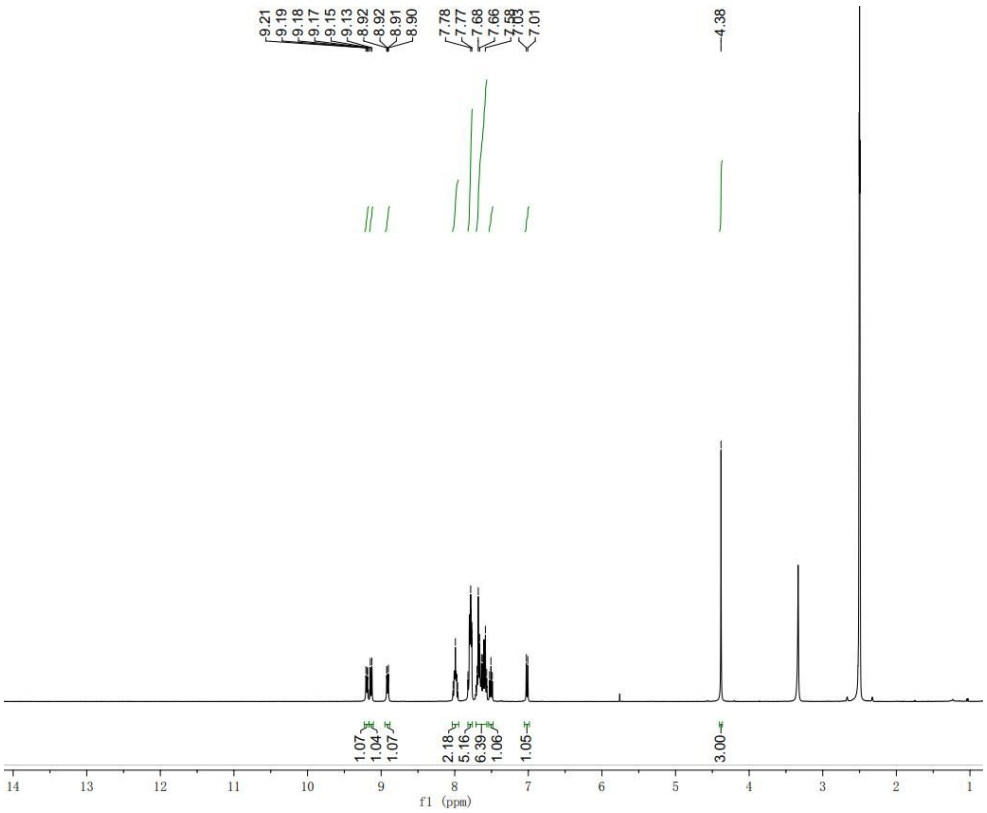


Figure S34. ^{1}H-NMR spectrum of MPPI-P. Solvent: DMSO-d_6.

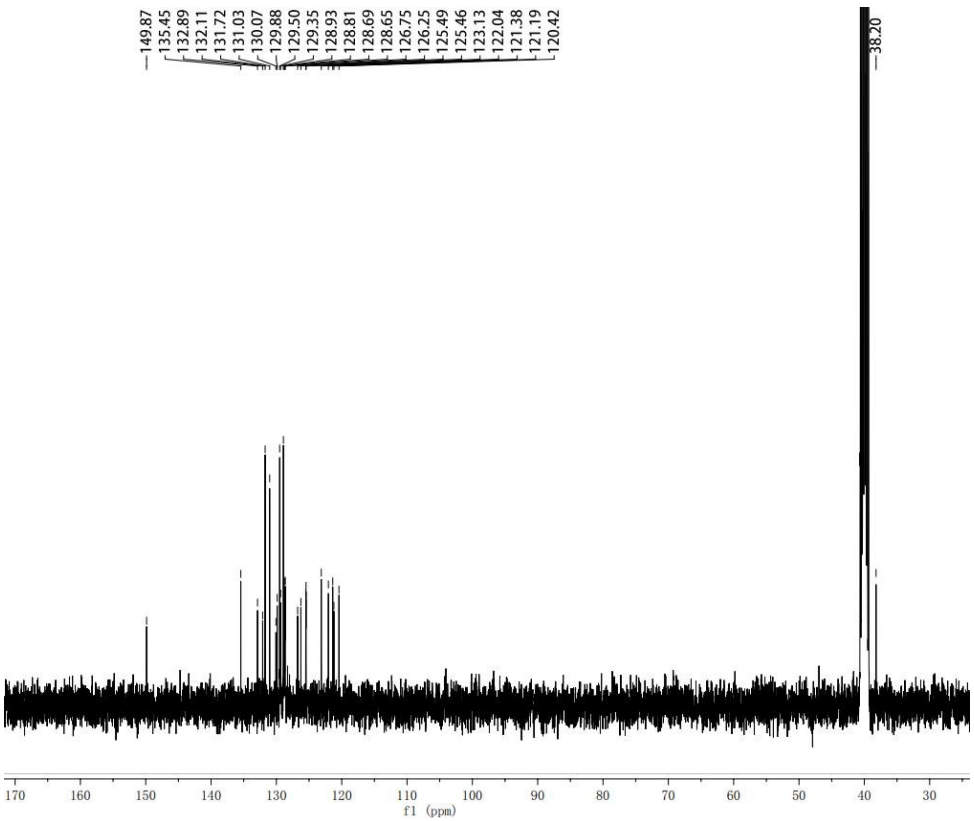


Figure S35. ^{13}C-NMR spectrum of MPPI-P. Solvent: DMSO-d_6.

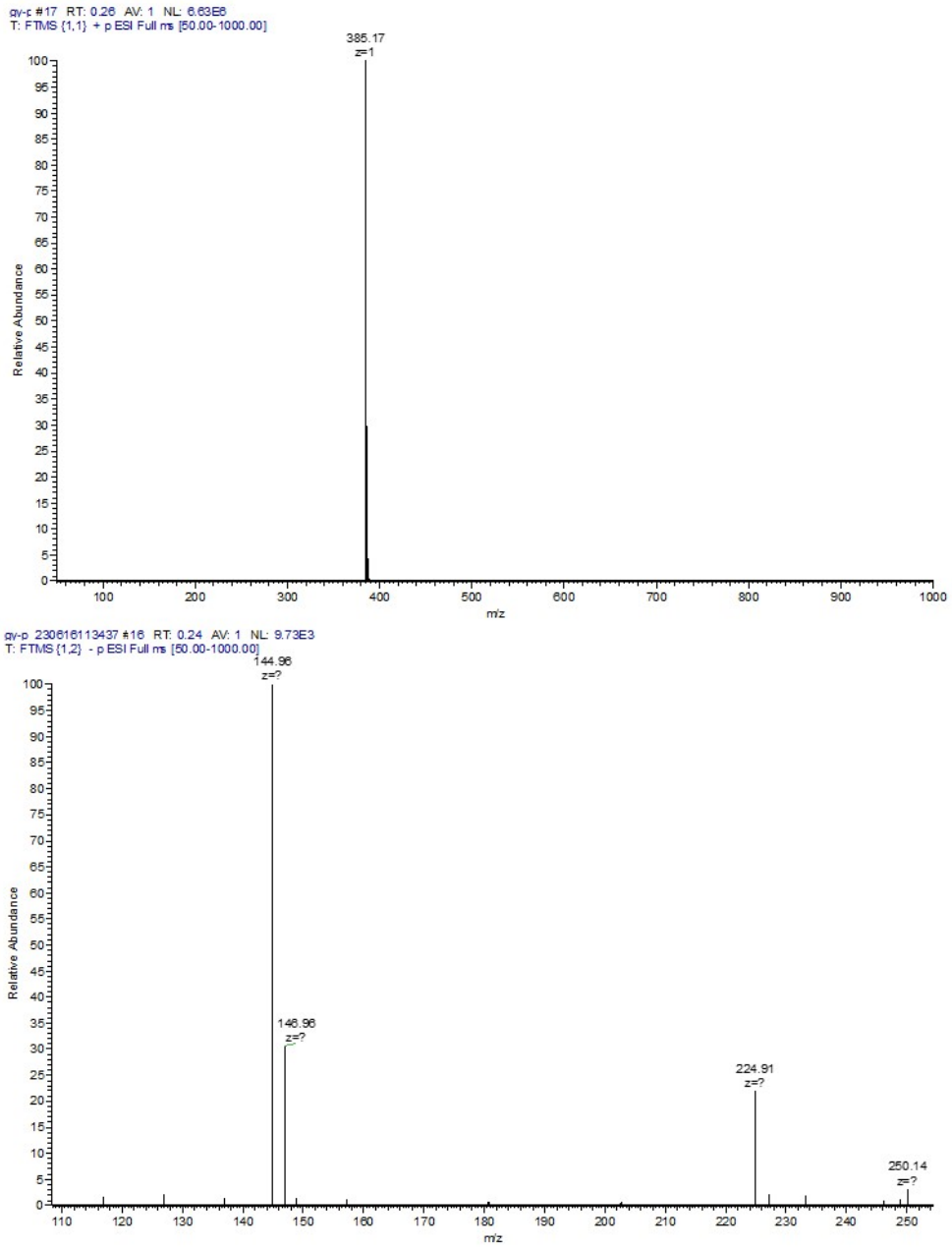


Figure S36. MS spectrum of MPPI-P.

4. Photophysical properties

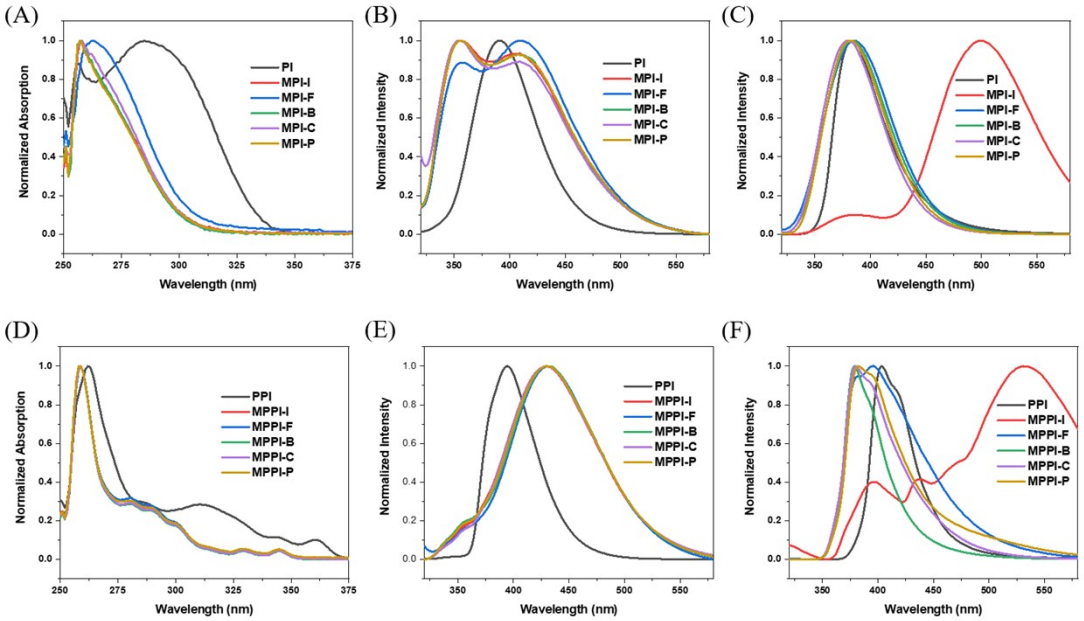


Figure 37. (A), (D) Normalized UV-visible absorption spectra of PI series and PPI series in DMSO. (B), (E) Normalized PL spectra of PI series and PPI series in DMSO (excitation wavelength: 300 nm, the concentrations were all 10^{-5} mol/L). (C), (F) Normalized PL spectra of PI series and PPI series in solid (excitation wavelength: 300 nm).

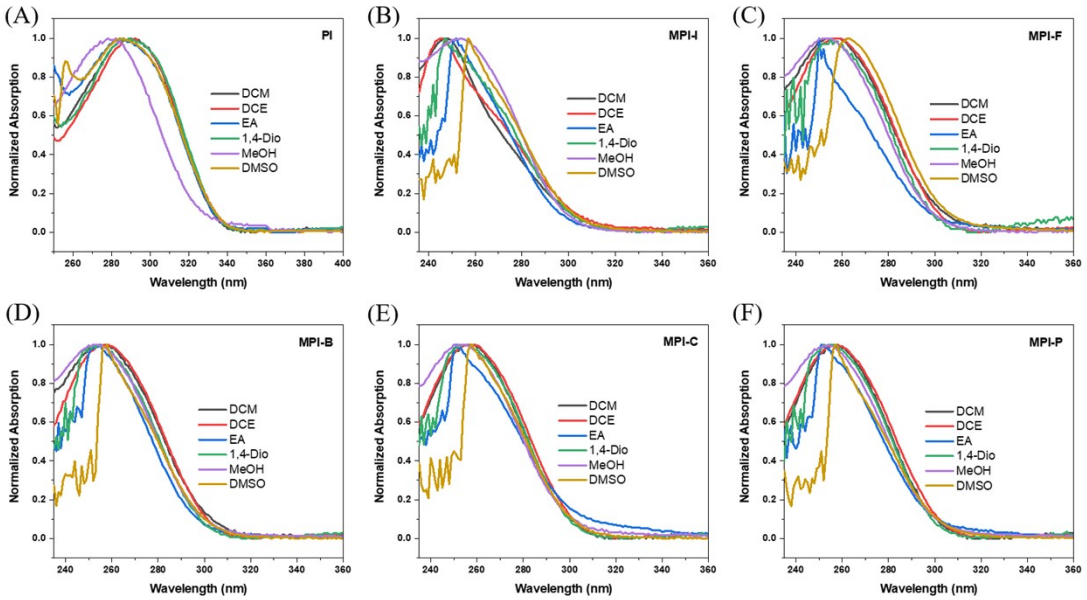


Figure S38. Normalized UV-visible absorption spectra of PI (A), MPI-I (B), MPI-F

(C), MPI-B (D), MPI-C (E) and MPI-P (F) in various solvents (The concentrations were all 10^{-5} mol/L). The abbreviation of solvent: DCM = dichloromethane, DCE = 1,2-dichloroethane, EA = ethyl acetate, 1,4-Dio = 1,4-dioxane, MeOH = methanol, DMSO = dimethyl sulfoxide.

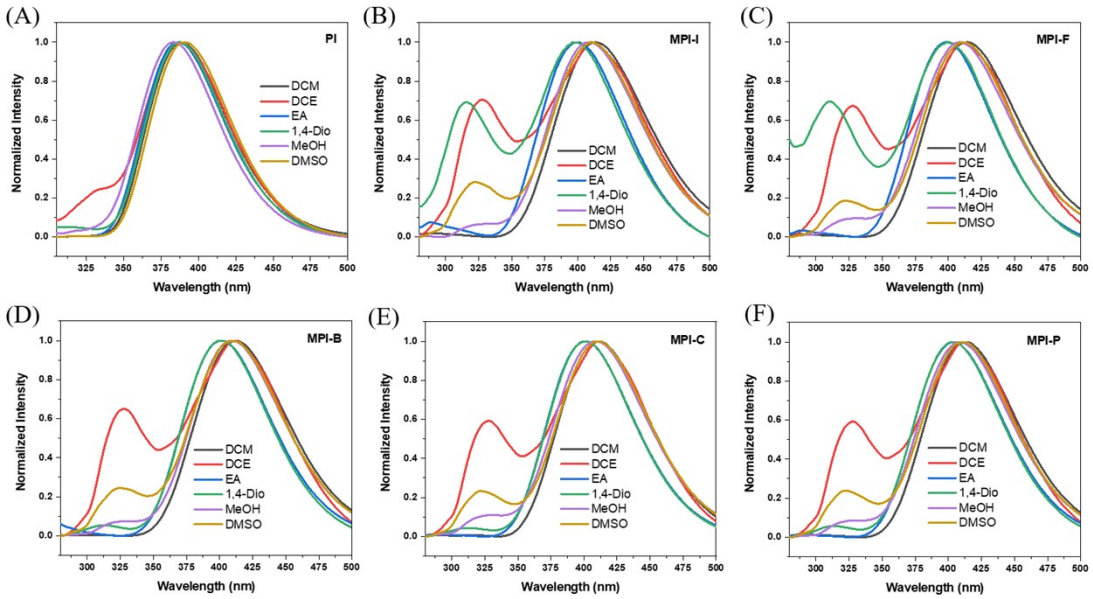


Figure S39. Normalized fluorescence spectra of PI (A), MPI-I (B), MPI-F (C), MPI-B (D), MPI-C (E) and MPI-P (F) in various solvents (The concentrations were all 10^{-5} mol/L; excitation wavelength: 285 nm for PI; 260 nm for MPI-I, MPI-F, MPI-B, MPI-C and MPI-P). The abbreviation of solvent: DCM = dichloromethane, DCE = 1,2-dichloroethane, EA = ethyl acetate, 1,4-Dio = 1,4-dioxane, MeOH = methanol, DMSO = dimethyl sulfoxide.

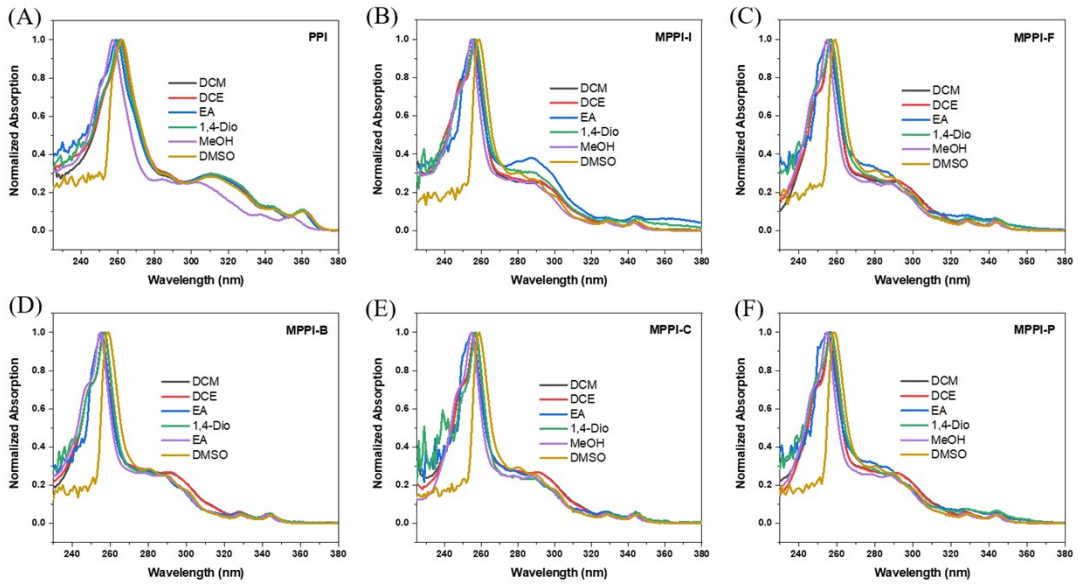


Figure S40. Normalized UV-visible absorption spectra of PPI (A), MPPI-I (B), MPPI-F (C), MPPI-B (D), MPPI-C (E) and MPPI-P (F) in various solvents (The concentrations were all 10^{-5} mol/L). The abbreviation of solvent: DCM = dichloromethane, DCE = 1,2-dichloroethane, EA = ethyl acetate, 1,4-Dio = 1,4-dioxane, MeOH = methanol, DMSO = dimethyl sulfoxide.

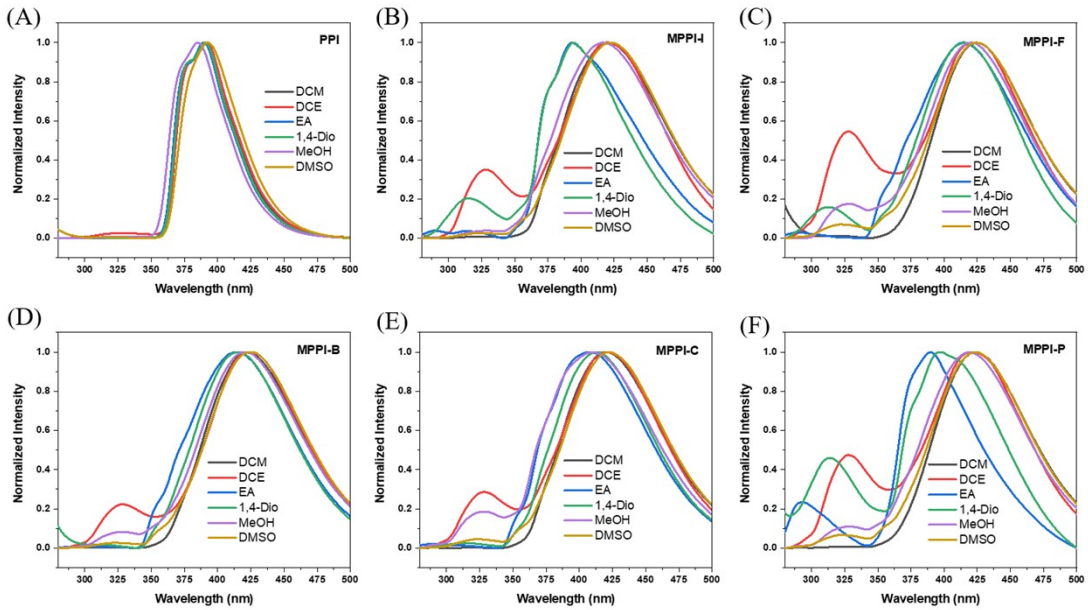


Figure S41. Normalized fluorescence spectra of PPI (A), MPPI-I (B), MPPI-F (C), MPPI-B (D), MPPI-C (E) and MPPI-P (F) in various solvents (The concentrations were all 10^{-5} mol/L; excitation wavelength: 260 nm for PPI, MPPI-I, MPPI-F, MPPI-B, MPPI-C and MPPI-P). The abbreviation of solvent: DCM = dichloromethane, DCE =

1,2-dichloroethane, EA = ethyl acetate, 1,4-Dio = 1,4-dioxane, MeOH = methanol, DMSO = dimethyl sulfoxide.

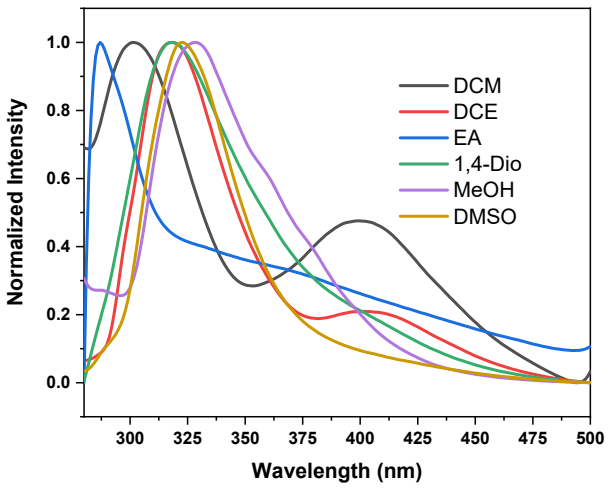


Figure S42. Normalized PL spectra of different solvents (The excitation wavelength: 260 nm). The abbreviation of solvent: DCM = dichloromethane, DCE = 1,2-dichloroethane, EA = ethyl acetate, 1,4-Dio = 1,4-dioxane, MeOH = methanol, DMSO = dimethyl sulfoxide.

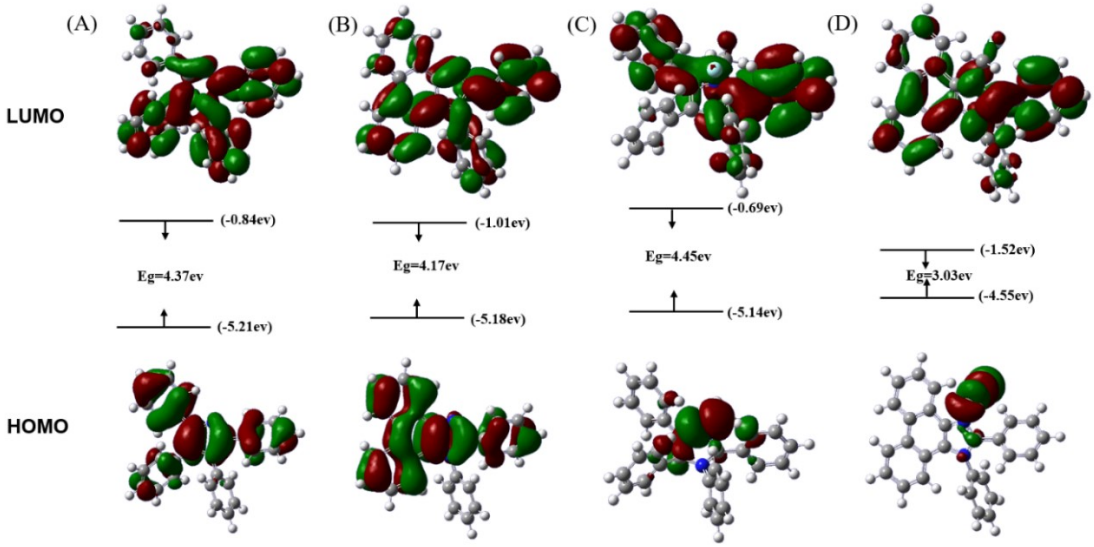


Figure S43. Molecular orbital and energy levels of PI (A), PPI (B), MPI-F (C) and MPPI-F (D). Molecular orbital amplitude plots of HOMO and LUMO energy levels calculated using the B3LYP/6-31G(d) basis set in the Gaussian 09 program. Eg (energy

gap) = LUMO - HOMO.

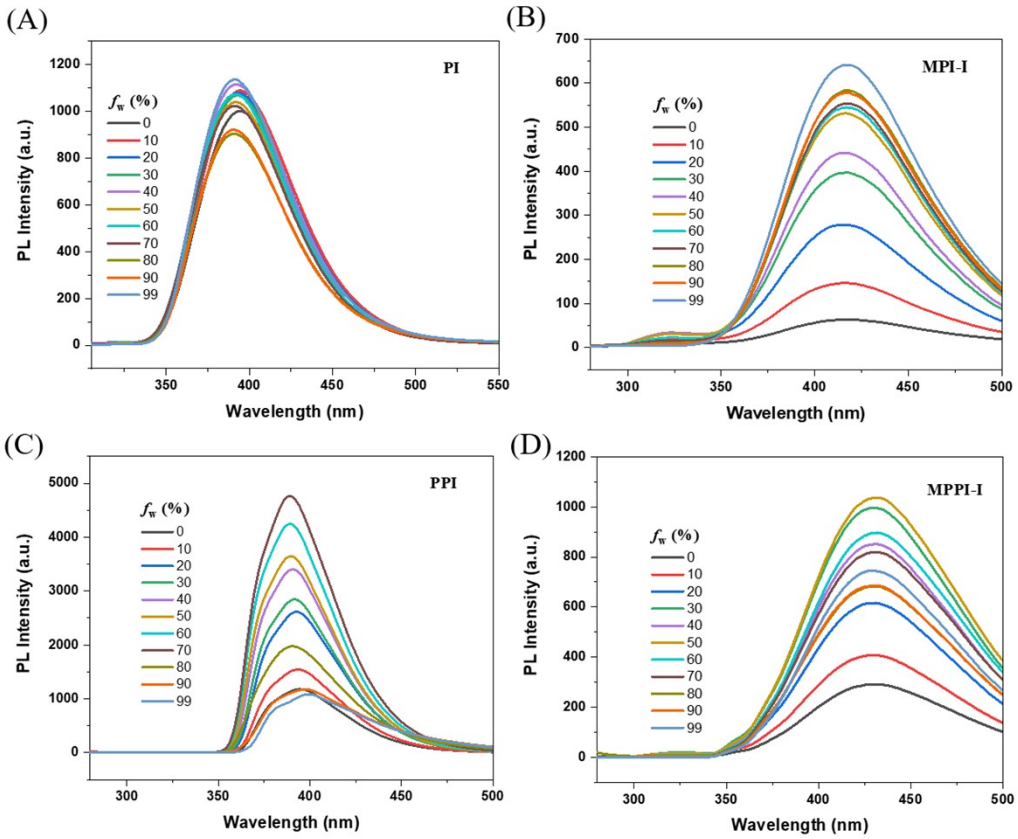


Figure 44. PL spectra of (A) PI, (B) MPI-I, (C) PPI and (D) MPPI-I in DMSO/water mixtures against different water fractions. Excitation wavelengths: 285 nm, 260 nm, and 260 nm, 260nm respectively; The concentrations were all 10^{-5} mol/L.

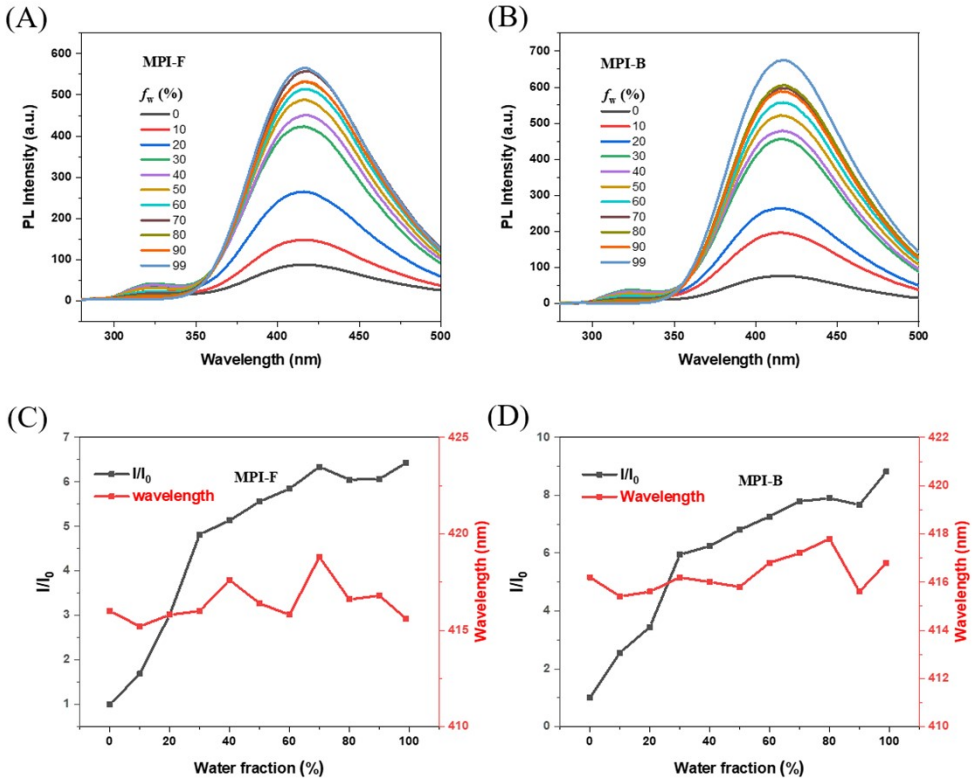


Figure S45. Fluorescence spectra of MPI-F (A) and MPI-B (B) against different volume fractions of water in DMSO/water mixture. Plot of relative maximum fluorescence intensity and wavelength of MPI-F (C) and MPI-B (D) upon different volume fractions of water. Excitation wavelengths: 260 nm; The concentrations were all 10^{-5} mol/L.

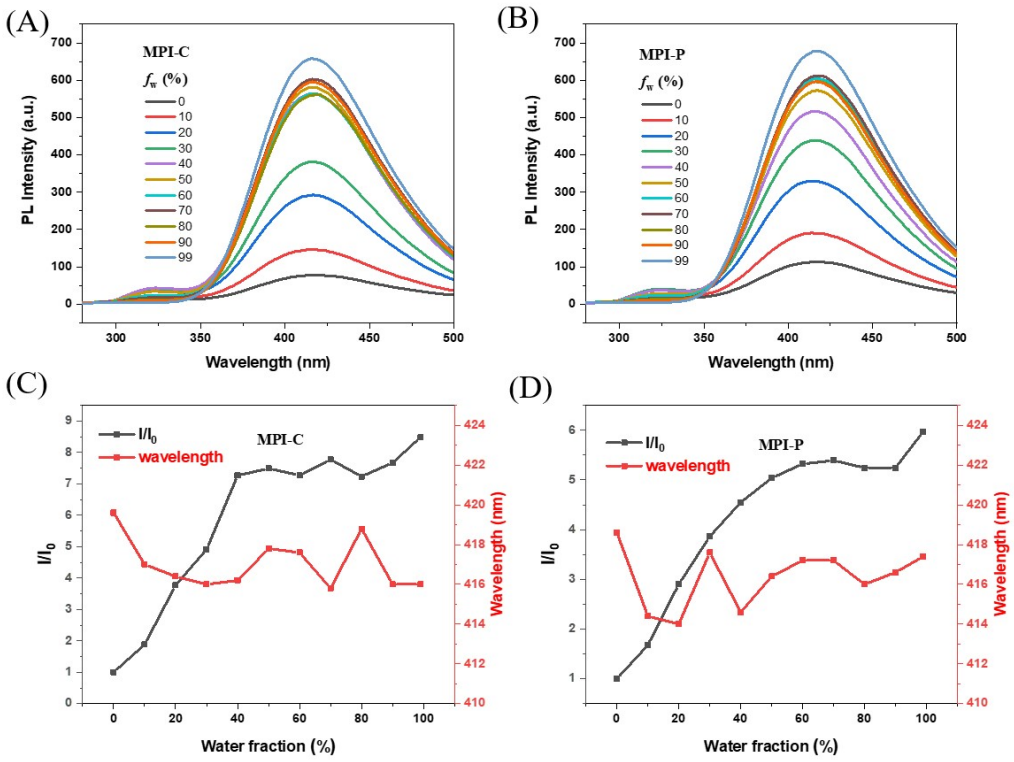


Figure S46. Fluorescence spectra of MPI-C (A) and MPI-P (B) against different volume fractions of water in DMSO/water mixture. Plot of relative maximum fluorescence intensity and wavelength of MPI-C (C) and MPI-P (D) upon different volume fractions of water. Excitation wavelengths: 260 nm; The concentrations were all 10^{-5} mol/L.

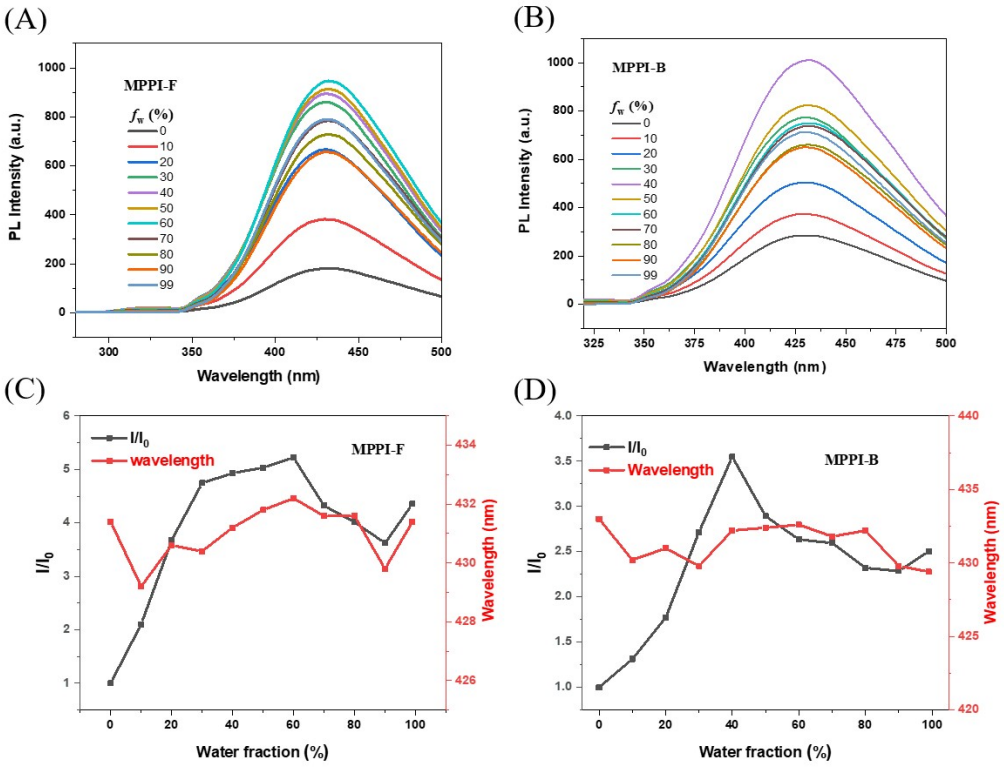


Figure S47. Fluorescence spectra of MPPI-F (A) and MPPI-B (B) against different volume fractions of water in DMSO/water mixture. Plot of relative maximum fluorescence intensity and wavelength of MPPI-F (C) and MPPI-B (D) upon different volume fractions of water. Excitation wavelengths: 260 nm; The concentrations were all 10^{-5} mol/L.

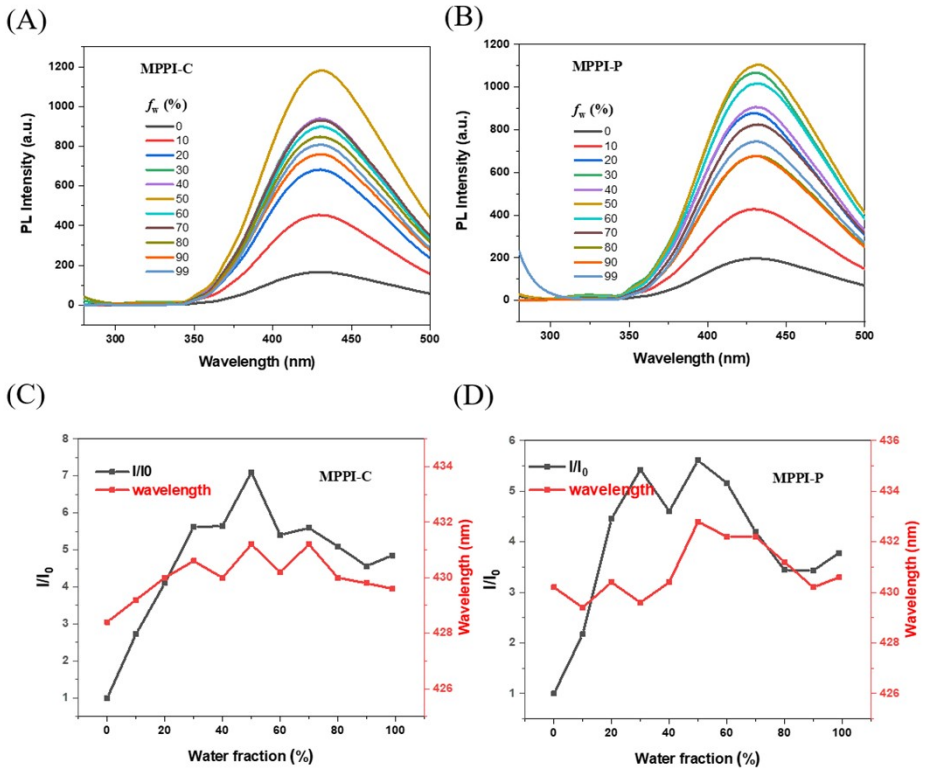


Figure S48. Fluorescence spectra of MPPI-C (A) and MPPI-P (B) against different volume fractions of water in DMSO/water mixture. Plot of relative maximum fluorescence intensity and wavelength of MPPI-C (D) and MPPI-P (D) upon different volume fractions of water. Excitation wavelengths: 260 nm; The concentrations were all 10^{-5} mol/L.

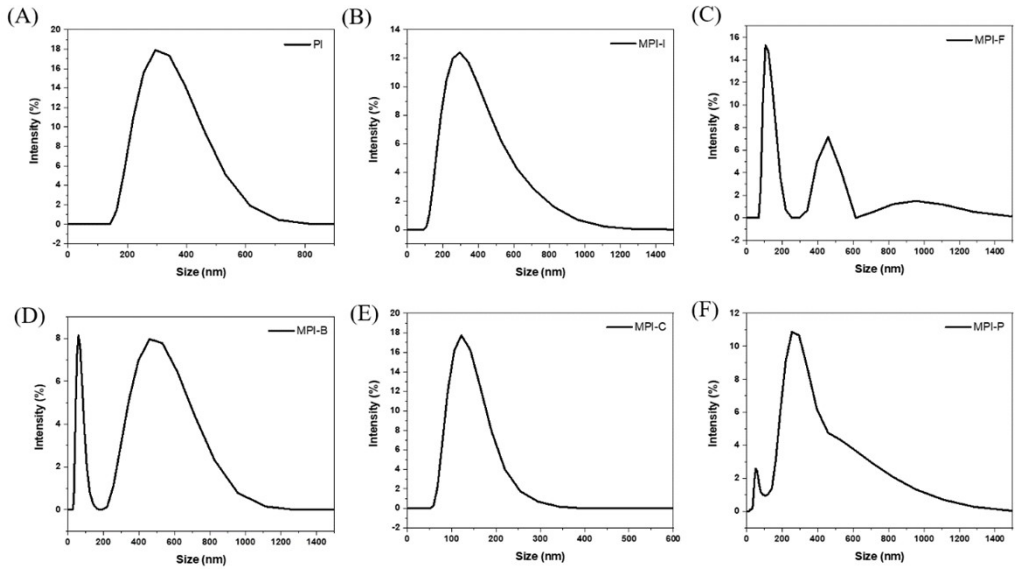


Figure S49. Particle diameter size distributions of PI (A), MPI-I (B), MPI-F (C), MPI-B (D), MPI-C (E), MPI-P (F) in DMSO/water mixture with 99% water fraction. The concentrations of compounds were all 10^{-5} mol/L.

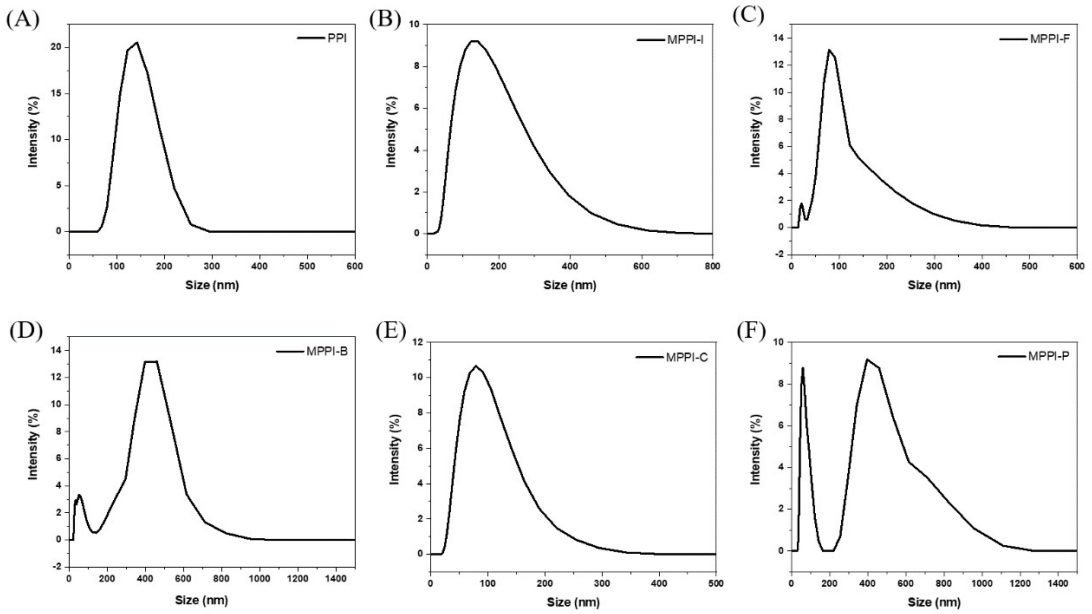


Figure S50. Particle diameter size distributions of PPI (A), MPPI-I (B), MPPI-F (C), MPPI-B (D), MPPI-C (E), MPPI-P (F) in DMSO/water mixture. The concentrations of compounds were all 10^{-5} mol/L. The water fraction in DMSO/water mixture: fw = 99 vol% for MPPI-I, MPPI-F, MPPI-B, MPPI-C, MPPI-P; fw = 70 vol% for PPI.

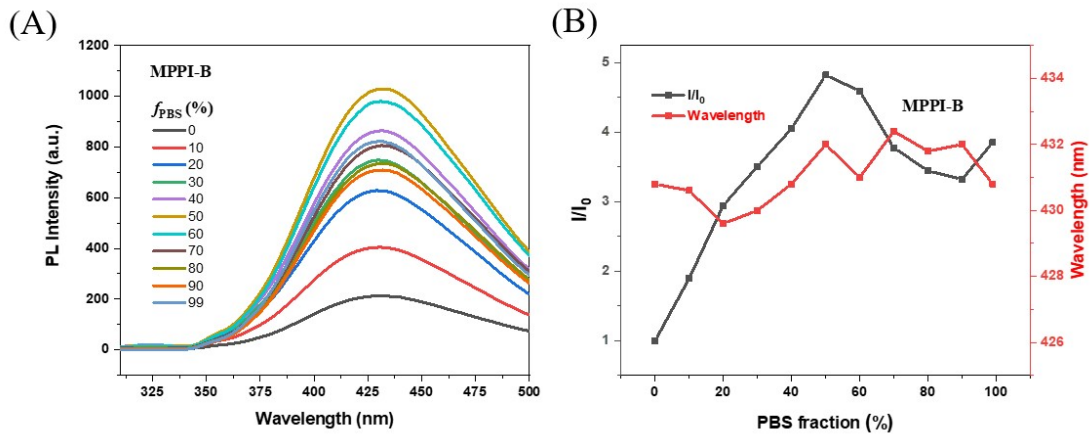


Figure S51. Fluorescence spectra of MPPI-B (A) against different volume fractions of PBS in DMSO/PBS mixture. Plot of relative maximum fluorescence intensity and wavelength of MPPI-B (B) upon different volume fractions of PBS. Excitation wavelengths: 260 nm; The concentrations were all 10^{-5} mol/L.

5. Single crystal structure

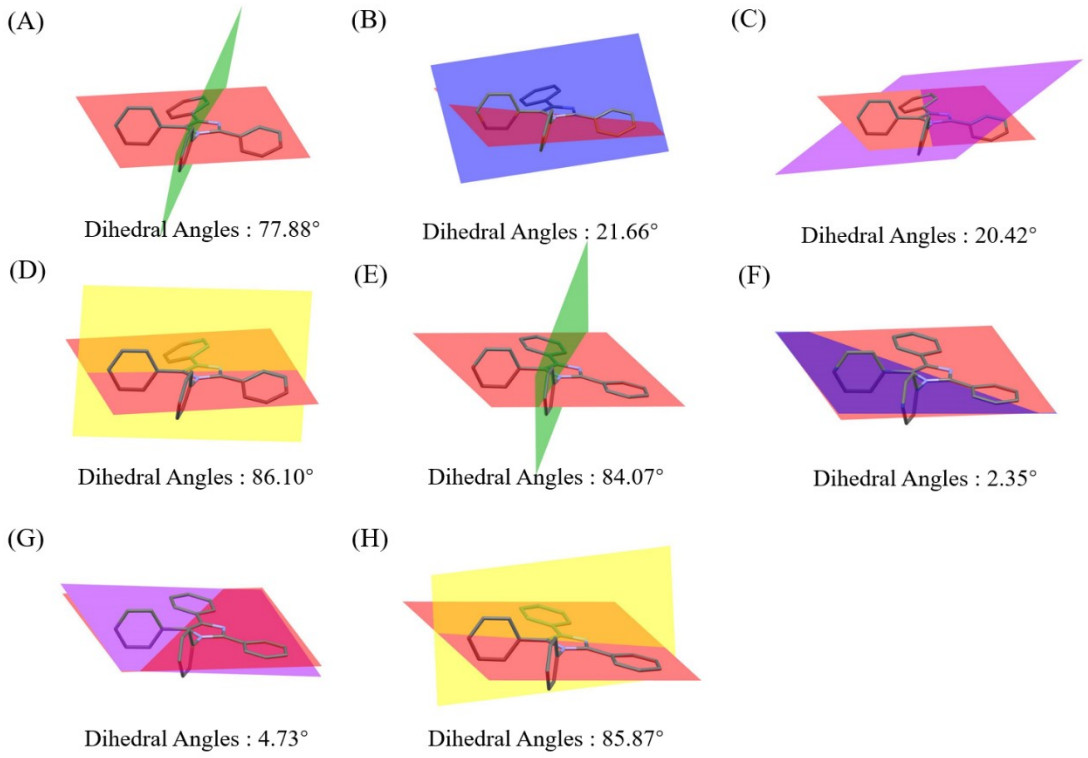


Figure S52. Dihedral angles between benzene and imidazole ring in PI. Group 1 (A, B, C and D), Group2 (E, F, G and H). (CCDC 2299928).

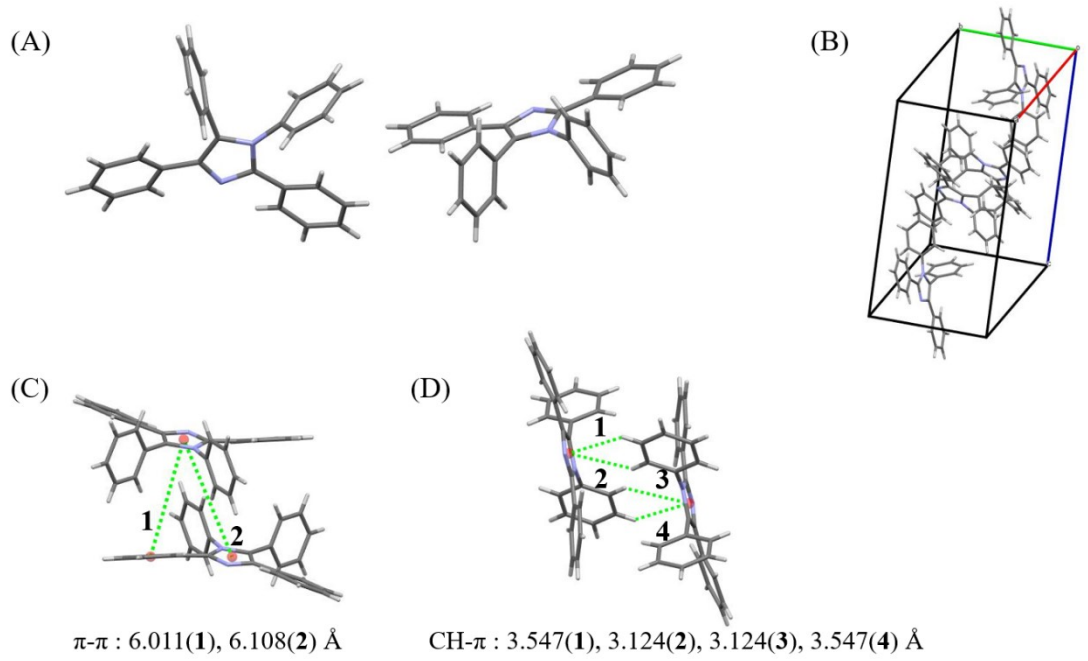


Figure S53. (A) Single crystal structure of PI. (B) Unit cell of PI. (C) Intermolecular π - π distance. (D) Intermolecular C-H-π interaction. (CCDC 2299928).

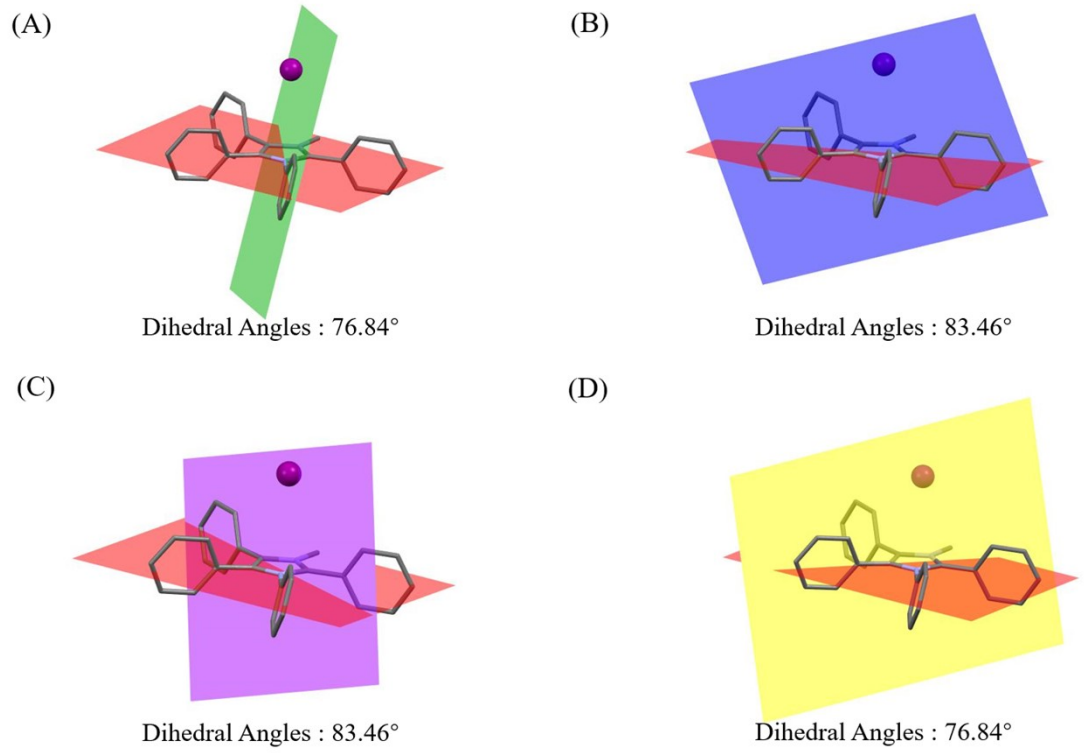


Figure S54. (A), (B), (C) and (D) Dihedral angles between four benzene and imidazole ring in MPI-I. (CCDC 2299930).

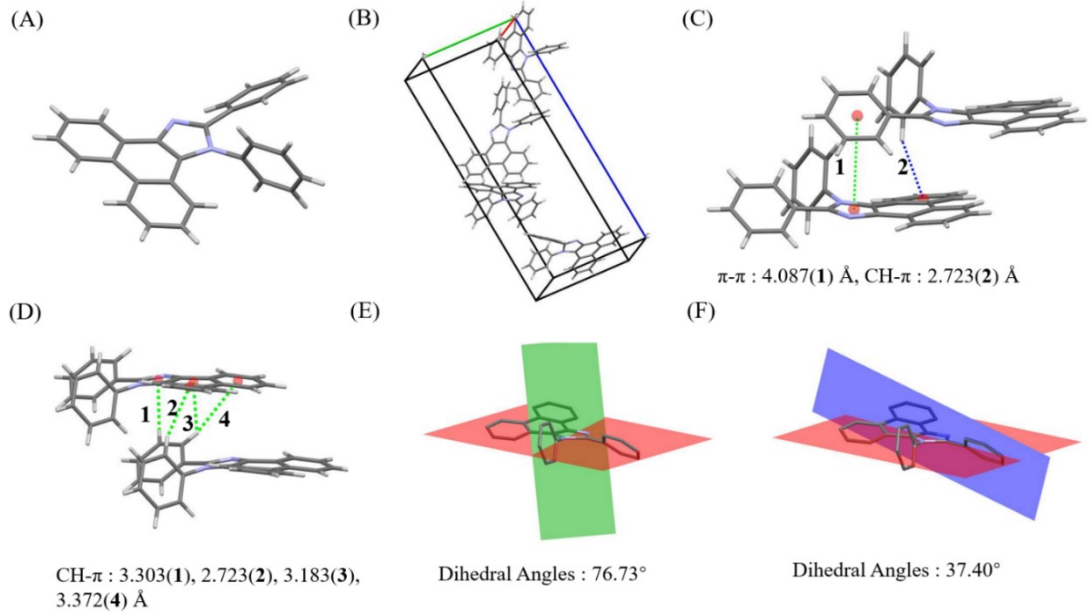


Figure S55. (A) Single crystal structure of PPI. (B) Unit cell of PPI. (C) Intermolecular π-π distance. (D) Intermolecular C-H-π interaction. (E) and (F) Dihedral angles between benzene and imidazole ring in PPI. (CCDC 2299929).

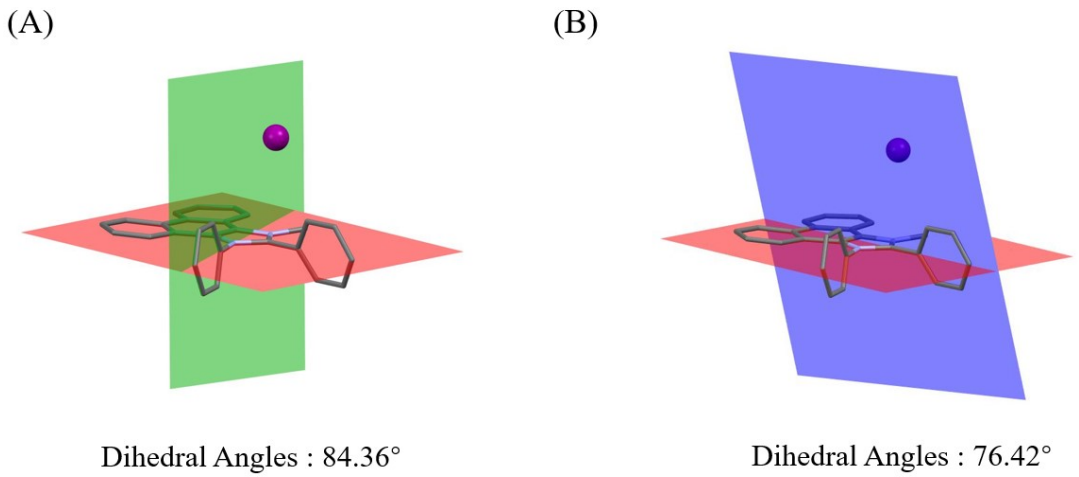


Figure S56. (A) and (B) Dihedral angles between benzene and imidazole ring in MPPI-I. (CCDC 2299931).

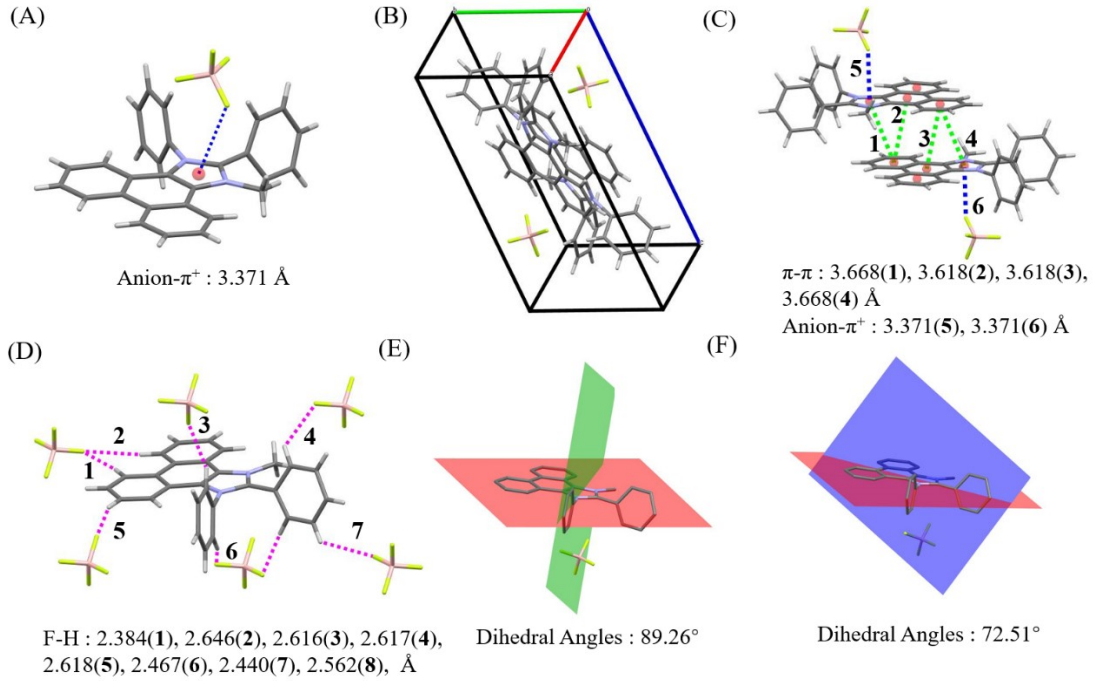


Figure S57. (A) Single crystal structure of MPPI-B. (B) Unit cell of MPPI-B. (C) Intermolecular π-π interaction. (D) C-H-F interaction. (E) and (F) Dihedral angles between benzene and imidazole ring. (CCDC 2301028).

Table S1. Crystallographic and structural refinement data of PI and PPI.

	PI	PPI

Empirical formula	$C_{27}H_{20}N_2$	$C_{27}H_{18}N_2$
Formula weight	372.45	370.43
Temperature/K	296(2)	170(2)
Crystal system	triclinic	orthorhombic
Space group	P-1	$P2_12_12_1$
a/Å	9.9299(15)	5.6802(5)
b/Å	10.0145(14)	12.0602(11)
c/Å	20.865(3)	27.607(3)
α/°	80.776(2)	90
β/°	82.041(2)	90
γ/°	82.681(2)	90
Volume/Å^3	2016.5(5)	1891.2(3)
Z	4	4
ρ_{calc}g/cm^3	1.227	1.301
μ/mm^{-1}	0.072	0.375
F(000)	784.0	776.0
Crystal size/mm^3	0.21×0.19×0.18	0.42×0.09×0.07
Radiation	MoKα(λ=0.71073)	GaKα(λ=1.34139)
2Θ range for data collection/°	3.984 to 54.866	5.57 to 114.348
Index ranges	-12≤h≤12, -9≤k≤12, -26≤l≤ 25	-7≤h≤6, -14≤k ≤15, -33≤l≤34
Reflections collected	12452	19750
Independent reflections	8896 [R_{int} = 0.0226, R_{sigma} = 0.0410]	3752 [R_{int} = 0.0821, R_{sigma} = 0.0678]
Data/restraints/parameters	8896/5/523	3752/0/262
Goodness-of-fit on F^2	1.132	1.112
Final R indexes [I>=2σ (I)]	R_1 = 0.0557, wR_2 = 0.1621	R_1 = 0.0748, wR_2 = 0.1911
Final R indexes [all data]	R_1 = 0.0828, wR_2 = 0.1818	R_1 = 0.0891, wR_2 = 0.1996
Largest diff. peak/hole / e Å^{-3}	0.29/-0.35	0.40/-0.29
Flack parameter		0.4(5)

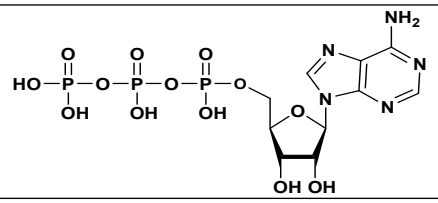
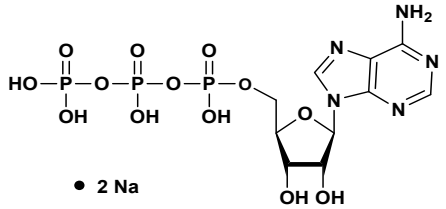
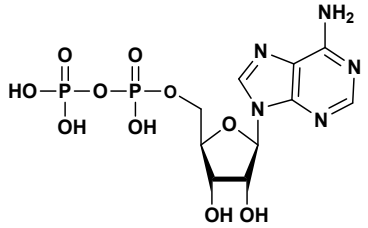
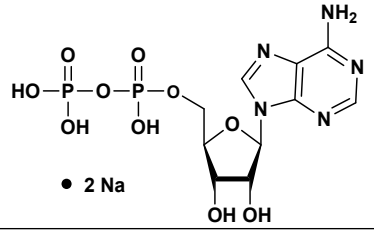
Table S2. Crystallographic and structural refinement data ofMPI-I, MPPI-I and MPPI-B.

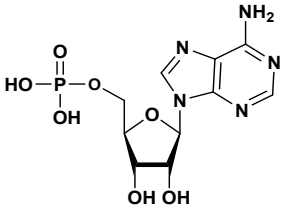
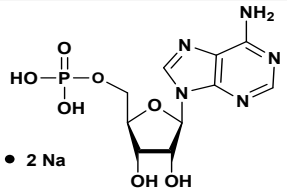
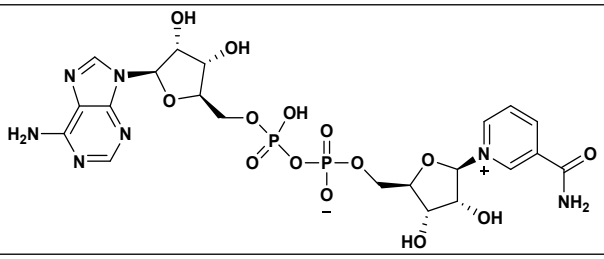
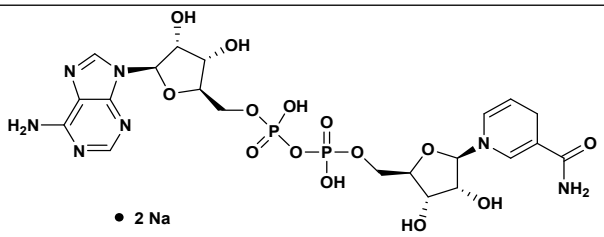
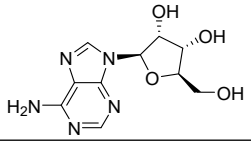
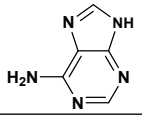
	MPI-I	MPPI-I	MPPI-B
Empirical formula	$C_{28}H_{23}IN_2$	$C_{28}H_{21}IN_2$	$C_{28}H_{21}BF_4N_2$
Formula weight	514.38	512.37	472.28
Temperature	300(2) K	296(2) K	302.15
Wavelength	1.54178 Å	0.71073 Å	
Crystal system	Orthorhombic	Monoclinic	triclinic
Space group	Ccca	$P2_1/c$	P-1
a	14.119(2) Å	13.712(6) Å	8.6240(2)
b	22.488(2) Å	10.149(4) Å	8.8580(2)
c	17.2094(19) Å	16.939(7) Å	15.8890(3)
α	90°	90°	94.467(2)
β	90°	105.859(10)°.	97.877(2)
γ	90°	90°	106.818(2)
Volume	5464.3(11) $Å^3$	2267.6(17) $Å^3$	1142.03(4)
Z	8	4	2
Density (calculated)	1.251 Mg/m^3	1.501 Mg/m^3	1.373
Absorption coefficient	9.308 mm^{-1}	1.430 mm^{-1}	0.860
F(000)	2064	1024	488.0
Crystal size	0.120×0.100×0.080 mm^3	0.120×0.100×0.080 mm^3	0.25×0.21×0.12
			CuKα(λ=1.54184)
Theta range for data collection	4.502 to 66.455°	2.364 to 25.166°	5.658 to 152.646
Index ranges	-16<=h<=14, -26<=k<=26, -20<=l<=20	-16<=h<=16, -12<=k<=12, -20<=l<=18	-6≤h≤10, -11≤k ≤11, -19≤l≤19
Reflections collected	19916	33041	21896
Independent reflections	2408 [R(int) = 0.1037]	4061 [R(int) = 0.1583]	4628 [R_{int} = 0.0297, R_{sigma} = 0.0234]
Completeness to theta = 25.166°	99.6 %	99.6 %	
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	

Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	
Data / restraints / parameters	2408 / 134 / 119	4061 / 0 / 282	4628/70/391
Goodness-of-fit on F2	1.040	1.021	1.078
Final R indices [I>2sigma(I)]	R1 = 0.1038, wR2 = 0.2205	R1 = 0.0785, wR2 = 0.1556	R_1 = 0.0521, wR_2 = 0.1553
R indices (all data)	R1 = 0.1628, wR2 = 0.2432	R1 = 0.2095, wR2 = 0.2074	R_1 = 0.0577, wR_2 = 0.1619
Extinction coefficient	0.00027(8)	0.0045(7)	
Largest diff. peak and hole	0.703 and -0.404 e.Å^{-3}	0.685 and -0.938 e.Å^{-3}	0.30/-0.26

6. Detection of adenine-containing biocompounds

Table S3. The name, structure and abbreviation of adenine-containing biocompounds.

Name	Structure	Abbreviation
Adenosine triphosphate		ATP
Adenosine triphosphate disodium salt		$ATPNa_2$
Adenosine diphosphate		ADP
Adenosine diphosphate disodium salt		$ADPNa_2$

Adenosine monophosphate		AMP
Adenosine monophosphate disodium salt		$AMPNa_2$
β-Nicotinamide adenine dinucleotide		NAD^+
β-Nicotinamide adenine dinucleotide, reduced disodium salt		$NADHNa_2$
Adenosine		Adenosine
Adenine		Adenine

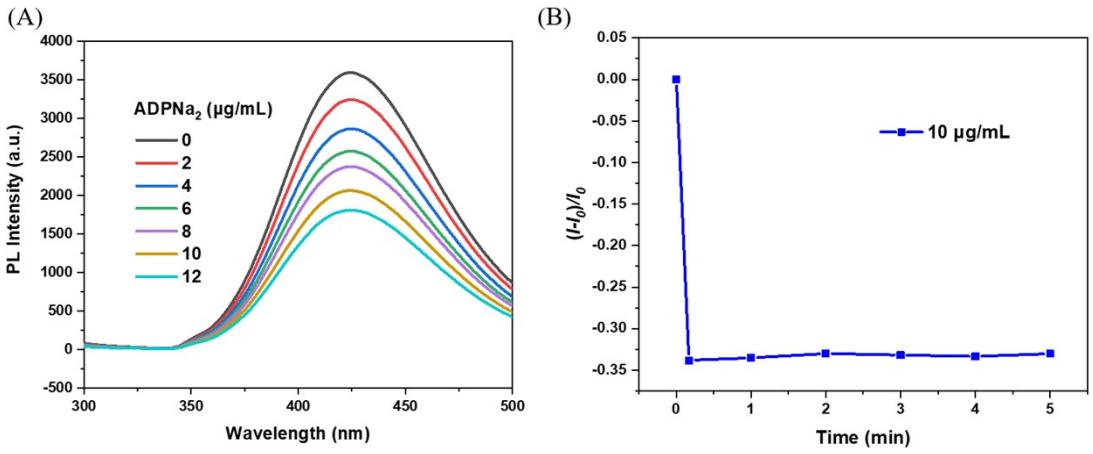


Figure S58. (A) PL intensity of MPPI-B (10^{-6} mol/L in DMSO/PBS mixture: 1/99 v/v)

against different $ADPNa_2$ concentrations (0-12 μg/mL). (B) Fluorescent response of MPPI-B (10^{-6} mol/L in DMSO/PBS mixture: 1/99 v/v) upon $ADPNa_2$ at different time. The excitation wavelength is 260 nm.

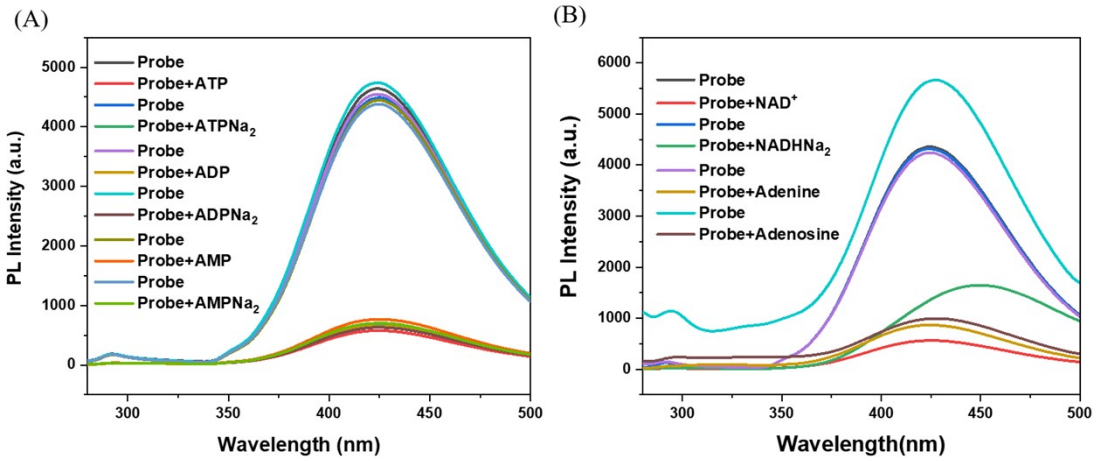


Figure S59. (A) PL spectra of Probe (MPPI-B) upon different adenosine derivatives (ATP, $ATPNa_2$, ADP, $ADPNa_2$, AMP, and $AMPNa_2$). (B) PL spectra of Probe (MPPI-B) upon adenosine and its derivatives (NAD^+, $NADHNa_2$, adenine and adenosine). The concentration of MPPI-B was 10^{-6} mol/L in DMSO/PBS (v/v: 1/99). The concentrations of ATP, $ATPNa_2$, ADP, $ADPNa_2$, AMP, $AMPNa_2$, NAD^+, $NADHNa_2$ and adenosine were all 10^{-4} mol/L in DMSO/PBS (v/v: 1/99), the concentration of adenine was 4.4×10^{-5} mol/L in DMSO/PBS (v/v: 1/99). The excitation wavelength is 260 nm.

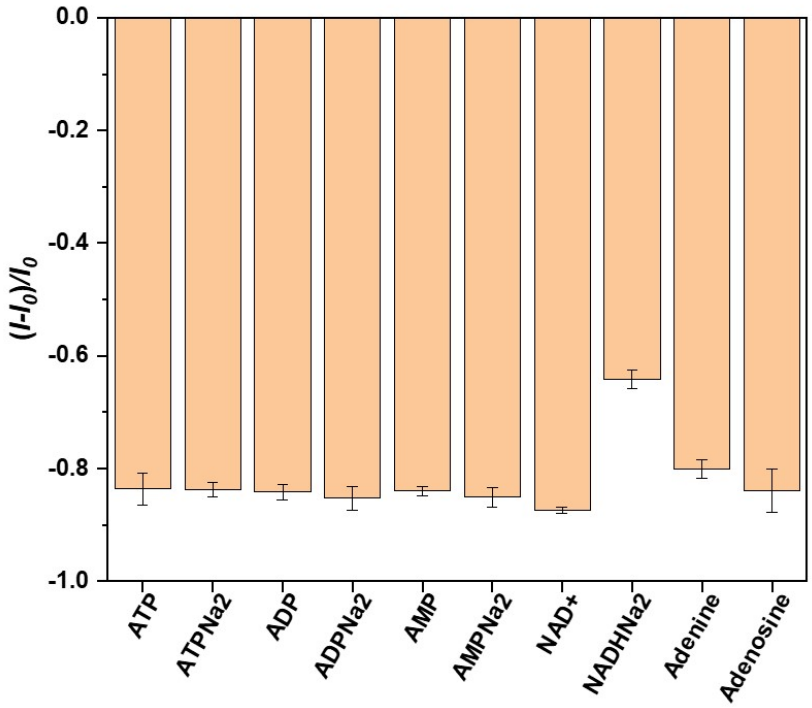


Figure S60. Relative fluorescence intensity versus different compounds. The concentration of MPPI-B was 10^{-6} mol/L in DMSO/PBS (v/v: 1/99). The concentrations of ATP, $ATPNa_2$, ADP, $ADPNa_2$, AMP, $AMPNa_2$, NAD^+, $NADHNa_2$ and adenosine were all 10^{-4} mol/L in DMSO/PBS (v/v: 1/99), the concentration of adenine was 4.4 ✍10^{-5} mol/L in DMSO/PBS (v/v: 1/99). The excitation wavelength was 260 nm.

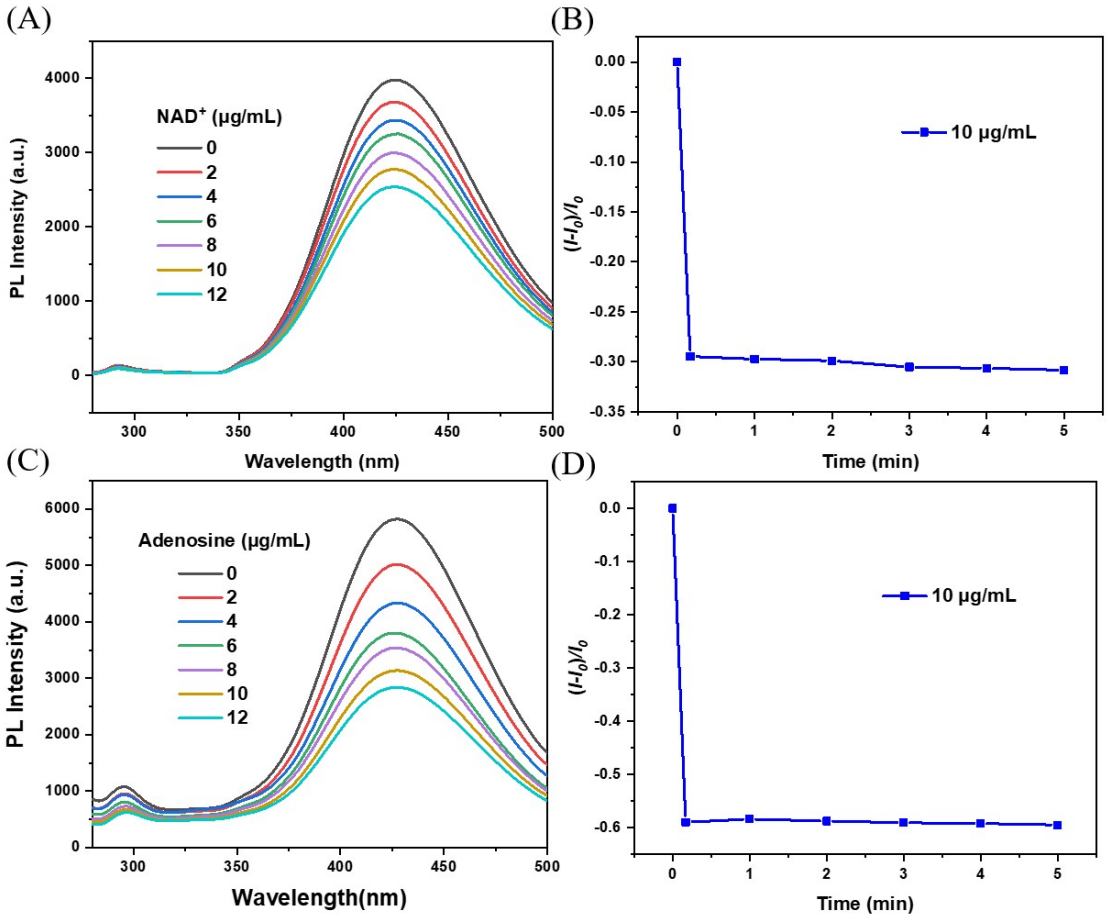


Figure S61. (A) PL intensity of MPPI-B (10^{-6} mol/L in DMSO/PBS mixture: 1/99 v/v) against different NAD^+ concentrations (0-12 μg/mL). (B) Fluorescent response of MPPI-B (10^{-6} mol/L in DMSO/PBS mixture: 1/99 v/v) upon NAD^+ at different time. (C) PL intensity of MPPI-B (10^{-6} mol/L in DMSO/PBS mixture: 1/99 v/v) against different adenosine concentrations (0-6 μg/mL). (D) Fluorescent response of MPPI-B (10^{-6} mol/L in DMSO/PBS mixture: 1/99 v/v) upon adenosine at different time. The excitation wavelength is 260 nm.

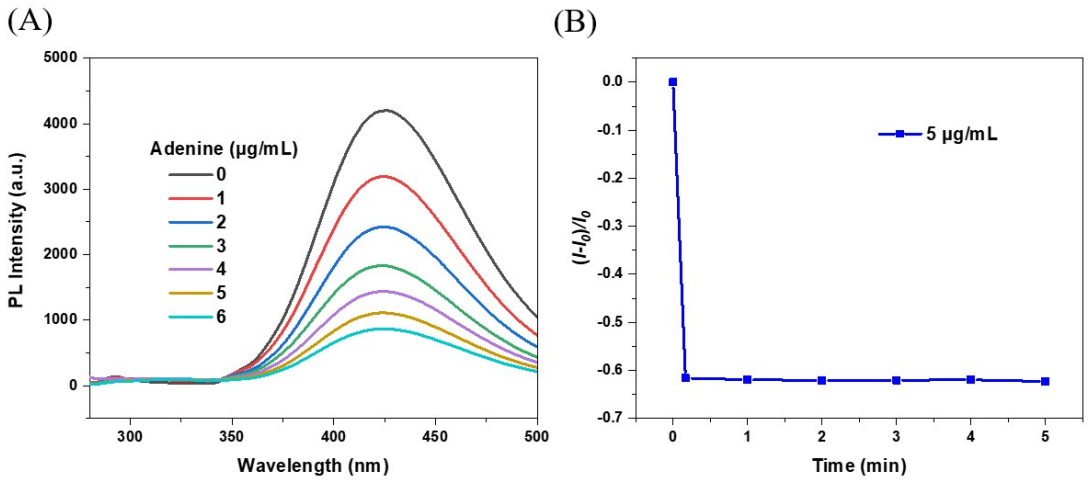


Figure S62. (A) PL intensity of MPPI-B (10^{-6} mol/L in DMSO/PBS mixture: 1/99 v/v) against different adenine concentrations (0-6 μg/mL). (B) Fluorescent response of MPPI-B (10^{-6} mol/L in DMSO/PBS mixture: 1/99 v/v) upon adenine at different time. The excitation wavelength is 260 nm.

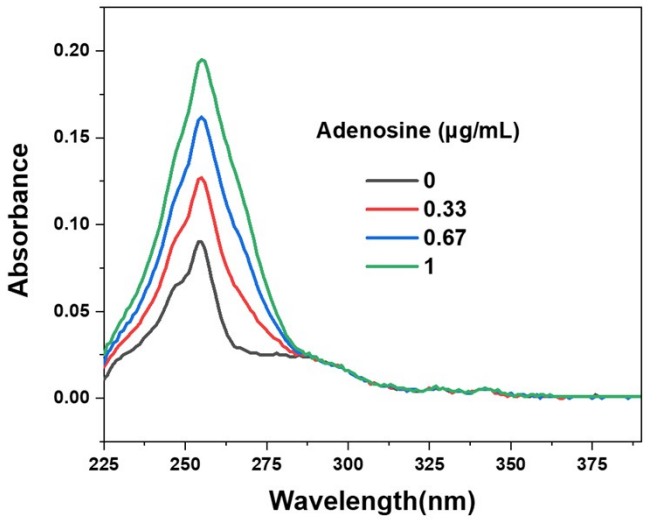


Figure S63. UV-visible absorption spectra of MPPI-B (10^{-5} mol/L in DMSO/PBS mixture: 1/99 v/v) against different adenosine derivatives concentrations (0-1 μg/mL).

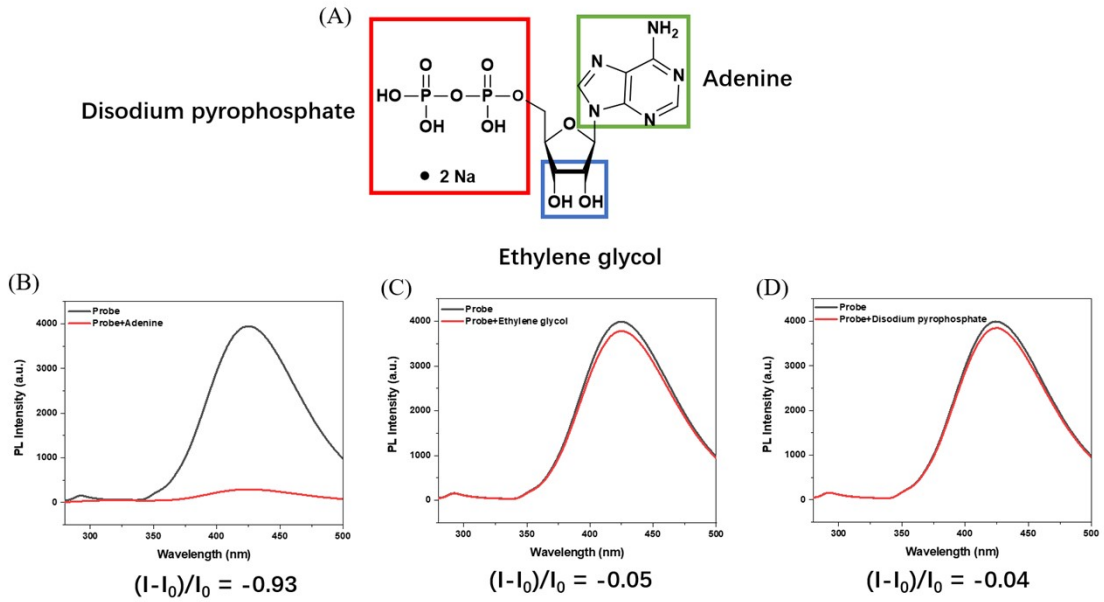


Figure S64. (A) Structure of $ADPNa_2$ and its corresponding functional groups. (B) PL spectra of MPPI-B before and after mixing with adenine. (C) PL spectra of MPPI-B before and after mixing with ethylene glycol. (D) PL spectra of MPPI-B before and after mixing with disodium pyrophosphate. The concentration of MPPI-B was 10^{-6} mol/L in DMSO/PBS (v/v: 1/99). The concentrations of adenine, ethylene glycol and disodium pyrophosphate were 20 μg/mL in DMSO/PBS (v/v: 1/99) respectively. The excitation wavelength is 260 nm.

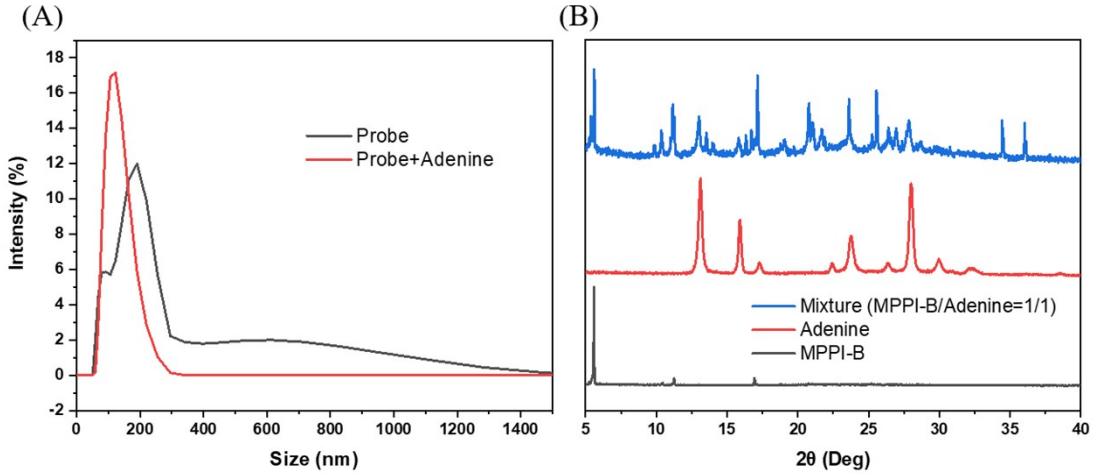


Figure S65. (A) Particle size distribution of MPPI-B before and after mixing with adenine, these aggregates were formed in the mixture of DMSO/H_2O (v/v: 1:99). (B) Normalized XRD curves of MPPI-B, adenine and their mixture, these samples were prepared by slow evaporation in methanol.