

Electronic Supplementary Information (ESI)

Room temperature multicomponent polymerizations of alkynes, sulfonyl azides, and *N*-protected isatins toward oxindoles-containing poly(*N*-acylsulfonamide)s

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Contents

Synthesis and characterization

Table S1 Solvent effect on the MCP of **1a**, **2**, and **3a**^a

Table S2 Base effect on the MCP of **1a**, **2**, and **3a**^a

Table S3 Effect of the concentration of CuI on the MCP of **1a**, **2**, and **3a**^a

Table S4 Temperature effect on the MCP of **1a**, **2**, and **3a**^a

Table S5 Monomer concentration effect on the MCP of **1a**, **2**, and **3a**^a

Table S6 Effect of time on the MCP of **1a**, **2**, and **3a**^a

Table S7 Effect of the amount of H₂O on the MCP of **1a**, **2**, **3c**, and H₂O^a

Table S8 Effect of time on the MCP of **1a**, **2**, **3c**, and H₂O^a

Table S9 Monomer concentration effect on the MCP of **1a**, **2**, **3c**, and water^a

Scheme S1 Synthesis of model compounds **6-8**.

Fig. S1 HR-MS spectrum of compound **6**.

Fig. S2 HR-MS spectrum of compound **7**.

Fig. S3 HR-MS spectrum of compound **8**.

Fig. S4 IR spectra of (A) **P2**, (B) **P3**, (C) **P4**, (D) **P5**, and (E) **P6**.

Fig. S5 IR spectra of (A) **7**, (B) **8**, and (C) **P7**.

Fig. S6 ^1H NMR spectra of (A) **P2**, (B) **P3**, (C) **P4**, (D) **P5**, and (E) **P6** in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

Fig. S7 ^{13}C NMR spectra of (A) **P2**, (B) **P3**, (C) **P4**, (D) **P5**, and (E) **P6** in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

Fig. S8 ^{13}C NMR spectra of (A) **7**, (B) **8**, and (C) **P7** in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

Fig. S9 PL spectra of **P5** in various solvents. Concentration: 10 μM . Excitation wavelength: 410 nm. Inset: fluorescent photographs of **P5** in different solvents taken under the illumination of a UV lamp (365 nm).

Synthesis and Characterization

Model reactions. The general procedure for the synthesis of model compounds **6** or **7** are shown below using the preparation of **6** as an example. Alkyne **4** (46 mg, 0.45 mmol) and sulfonyl azide **5** (88 mg, 0.45 mmol) were added sequentially to a mixture of **3a** (48 mg, 0.30 mmol), LiOH (9 mg, 0.36 mmol), CuI (6 mg, 0.03 mmol), and $(\text{C}_2\text{H}_5)_4\text{NI}$ (8 mg, 0.03 mmol) in a combined solvent of DCM (3 mL) and *t*-BuOH (0.3 mL) under N_2 at 30 $^\circ\text{C}$. The reaction mixture was stirred for 6 h which was then quenched with saturated NH_4Cl (10 mL), extracted with ethyl acetate (10×3 mL), and dried over anhydrous Na_2SO_4 . The residue was purified by flash column chromatography on silica gel with hexane/acetone ($v/v = 3:1$) to give compound **6**.

The procedure for the synthesis of model compound **8** is given below. Alkyne **4** (46 mg, 0.45 mmol), sulfonyl azide **5** (88 mg, 0.45 mmol), and H_2O (162 mg, 9 mmol) were added sequentially to a mixture of **3c** (67 mg, 0.30 mmol), Na_2CO_3 (38 mg, 0.36 mmol), CuI (6 mg, 0.03 mmol), and $(\text{C}_2\text{H}_5)_4\text{NI}$ (8 mg, 0.03 mmol) in 3 mL anhydrous DMF under N_2 at 30 $^\circ\text{C}$. The reaction mixture was stirred for 1.5 h which was then quenched with saturated NH_4Cl (10 mL), extracted with ethyl acetate (10×3 mL), and dried over anhydrous Na_2SO_4 . The residue was purified by column chromatography on silica gel with hexane/acetone ($v/v = 4:1$) as an eluent to afford **8**.

Compound 6: a yellow solid was obtained in 82% yield. IR (KBr thin film), ν (cm^{-1}): 3248 (N-H), 3059, 2929, 2865, 1702 (C=O), 1608, 1469, 1429, 1341, 1250, 1153, 856, 751, 699. ^1H NMR (500 MHz, $\text{DMSO-}d_6$), δ (ppm): 12.58 (s, 1H, N-H), 7.80 (d, $J = 7.5$ Hz, 2H), 7.55 – 7.49 (m, 3H), 7.42 – 7.35 (m, 4H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.00 (d, $J = 7.8$ Hz, 1H), 6.74 (t, $J = 7.6$ Hz, 1H), 6.45 (d, $J = 7.3$ Hz, 1H), 3.13 (s, 3H, N- CH_3), 2.40 (s, 3H, Ar- CH_3). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 165.77 (NH-C=O), 143.76, 139.81, 137.29, 129.26, 129.15, 129.02, 128.48, 128.08, 127.06, 122.26, 122.02, 121.40, 108.71, 26.09 (N- CH_3), 21.38 (Ar- CH_3). HRMS: m/z 455.1044 ($\text{M} + \text{Na}^+$, calcd 455.1041), 477.0869 ($\text{M} + 2\text{Na}^+ - \text{H}^+$, calcd 477.0861).

Compound 7: a yellow solid was obtained in 80% yield. IR (KBr thin film), ν (cm^{-1}): 3248 (N-H), 3057, 2923, 2856, 1709 (C=O), 1606, 1496, 1465, 1419, 1369, 1344, 1164, 1087, 853, 749, 701. ^1H NMR (500 MHz, $\text{DMSO-}d_6$), δ (ppm): 12.63 (s, 1H, N-H), 7.78 (d, $J = 8.1$ Hz, 2H), 7.65 – 7.47 (m, 6H), 7.47 – 7.41 (m, 4H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.23 (t, $J = 7.9, 1.0$ Hz, 1H), 6.81 (t, $J = 11.2, 4.2$ Hz, 1H), 6.74 (d, $J = 7.9$ Hz, 1H), 6.56 (d, $J = 7.7$ Hz, 1H), 2.36 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 164.93 (NH-C=O), 144.53, 134.21, 131.41, 130.52, 130.20, 129.84, 129.78, 128.73, 128.10, 127.19, 123.51, 122.91, 120.44, 109.99, 21.55 (CH_3). HRMS: m/z 517.1193 ($\text{M} + \text{Na}^+$, calcd 517.1198), 539.0958 ($\text{M} + 2\text{Na}^+ - \text{H}^+$, calcd 539.1017).

Compound 8: a white solid was obtained in 65% yield. IR (KBr thin film), ν (cm^{-1}): 3431 (-OH), 3247 (N-H), 3062, 2922, 2869, 1722 (C=O), 1697 (C=O), 1613, 1501, 1465, 1432, 1332, 1171, 1087, 899, 758, 699, 661. ^1H NMR (500 MHz, $\text{DMSO-}d_6$), δ (ppm): 12.31 (1H, N-H), 7.73 (d, $J = 8.3$ Hz, 1H), 7.69 (d, $J = 8.3$ Hz, 1H), 7.59 – 7.31 (m, 6H), 7.26 – 7.00 (m, 5H), 6.88 – 6.67 (m, 3H), 6.60 – 6.47 (m, 1H), 6.30 – 6.04 (m, 1H), 4.45 (s, 0.4H, -CH-), 4.35 (s, 0.6H, -CH-), 2.41 (s, 1.2H, CH_3), 2.39 (s, 1.8H, CH_3). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$), δ (ppm): 176.80 (NH-C=O), 175.44 (NH-C=O), 144.54, 143.97, 143.76, 141.48, 134.54, 134.16, 130.64, 130.11, 129.97, 129.90, 128.54, 128.18, 127.94, 127.88, 127.02, 126.72, 125.78, 122.74, 122.27, 109.09, 108.64, 78.08 (-C-), 75.39 (-C-), 58.72 (-CH-), 58.04 (-CH-), 21.64 (CH_3), 21.55 (CH_3). HRMS: m/z 535.1307 ($\text{M} + \text{Na}^+$, calcd 535.1304).

P1: a yellow powder was obtained in 98% yield. $M_w = 19\,300$ g/mol, $M_w/M_n = 1.78$. IR (KBr), ν (cm^{-1}): 3231 (N-H), 3062, 2950, 2926, 2859, 1709 (C=O), 1608, 1487, 1466, 1340, 1245, 1160, 875, 746, 695. ^1H NMR (500 MHz, DMSO- d_6), δ (ppm): 12.65 (N-H), 8.02, 7.55, 7.44, 7.26, 6.99, 6.64, 6.58, 3.13 (CH₃), 1.95 (CH₂), 1.01 (CH₂), 0.62 (CH₂, CH₃). ^{13}C NMR (125 MHz, DMSO- d_6), δ (ppm): 165.50 (NH-C=O), 160.02, 151.74, 144.96, 142.30, 141.78, 134.82, 133.60, 131.40, 131.07, 128.74, 127.31, 126.15, 124.66, 123.35, 122.95, 121.86, 120.49, 119.38, 119.09, 109.60, 55.75 (-C-), 26.43 (CH₂), 26.28 (CH₃), 22.92 (CH₂), 14.25 (CH₃).

P1': a yellow powder was obtained in 98% yield. $M_w = 19\,600$ g/mol, $M_w/M_n = 1.79$. IR (KBr), ν (cm^{-1}): 3064, 2929, 2862, 1707 (C=O), 1606, 1580, 1488, 1466, 1377, 1342, 1245, 1158, 1089, 873, 697. ^1H NMR (500 MHz, DMSO- d_6), δ (ppm): 7.94, 7.84, 7.63, 7.48, 7.42, 7.16, 6.94, 6.56, 6.49, 3.16 (CH₃), 1.91 (CH₂), 1.00 (CH₂), 0.59 (CH₂, CH₃). ^{13}C NMR (125 MHz, DMSO- d_6), δ (ppm): 165.25 (NH-C=O), 159.87, 151.74, 144.03, 142.51, 141.75, 134.69, 133.64, 132.24, 131.01, 128.71, 127.29, 125.76, 124.61, 123.40, 123.08, 121.82, 120.54, 119.35, 117.68, 110.19, 55.78 (-C-), 26.44 (CH₂), 26.30 (CH₃), 22.93 (CH₂), 14.26 (CH₃).

P2: a yellow powder was obtained in 98% yield. $M_w = 27\,600$ g/mol, $M_w/M_n = 1.53$. IR (KBr), ν (cm^{-1}): 3231 (N-H), 3076, 2956, 2929, 2856, 1709 (C=O), 1606, 1580, 1486, 1466, 1351, 1247, 1160, 1089, 873, 751, 697. ^1H NMR (500 MHz, DMSO- d_6), δ (ppm): 12.69 (N-H), 8.09, 8.03, 7.60, 7.45, 7.40, 7.28, 6.96, 6.64, 5.84 (CH), 5.20 (CH₂), 4.32 (CH₂), 1.97 (CH₂), 1.02 (CH₂), 0.63 (CH₂, CH₃). ^{13}C NMR (125 MHz, DMSO- d_6), δ (ppm): 165.27 (NH-C=O), 160.09, 151.75, 144.04, 143.61, 141.84, 133.53, 132.26, 131.06, 130.24, 128.75, 128.29, 127.30, 125.88, 124.68, 123.41, 123.08, 121.89, 120.60, 119.36, 117.69, 116.37, 110.19, 55.79 (-C-), 41.81 (CH₂), 26.44 (CH₂), 22.94 (CH₂), 14.27 (CH₃).

P3: a yellow powder was obtained in 97% yield. $M_w = 30\,600$ g/mol, $M_w/M_n = 1.95$. IR (KBr), ν (cm^{-1}): 3234 (N-H), 3062, 2955, 2928, 2861, 1714 (C=O), 1606, 1580, 1464, 1371, 1244, 1161, 1087, 873, 751, 698. ^1H NMR (500 MHz, DMSO- d_6), δ (ppm): 12.69 (N-H), 8.14, 8.00, 7.93, 7.68, 7.55, 7.42, 7.24, 7.13, 6.77, 6.72, 2.02 (CH₂), 1.04 (CH₂),

0.65 (CH₂, CH₃). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (ppm): 165.04 (NH-C=O), 159.35, 151.71, 144.41, 141.86, 134.32, 130.68, 130.13, 128.57, 127.12, 124.68, 123.24, 119.00, 109.91, 55.82 (-C-), 26.48 (CH₂), 22.99 (CH₂), 14.30 (CH₃).

P4: a yellow powder was obtained in 94% yield. $M_w = 17\ 200$ g/mol, $M_w/M_n = 1.83$. IR (KBr), ν (cm⁻¹): 3234 (N-H), 3059, 2932, 2879, 1706 (C=O), 1606, 1580, 1488, 1469, 1375, 1341, 1247, 1157, 1090, 873, 750, 698. ¹H NMR (500 MHz, DMSO-*d*₆), δ (ppm): 12.64 (N-H), 7.99, 7.89, 7.68, 7.41, 7.25, 7.18, 7.06, 6.81, 6.62, 6.37, 3.07 (CH₃). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (ppm): 165.44 (NH-C=O), 160.10, 144.85, 143.07, 141.18, 132.01, 131.20, 128.63, 128.52, 127.93, 127.42, 124.69, 123.12, 122.04, 119.24, 109.18, 26.14 (CH₃).

P5: a yellow powder was obtained in 97% yield. $M_w = 21\ 100$ g/mol, $M_w/M_n = 2.17$. IR (KBr), ν (cm⁻¹): 3228 (N-H), 3059, 2935, 2865, 1704 (C=O), 1606, 1585, 1488, 1375, 1338, 1250, 1158, 1090, 873, 752, 697. ¹H NMR (500 MHz, DMSO-*d*₆), δ (ppm): 12.62 (N-H), 8.02, 7.89, 7.87, 7.69, 7.52, 7.43, 7.40, 7.27, 7.21, 7.07, 6.98, 6.89, 6.86, 3.10 (CH₃). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (ppm): 165.66 (NH-C=O), 159.99, 148.62, 146.40, 144.69, 134.30, 131.05, 130.60, 130.07, 128.68, 126.57, 125.66, 124.67, 123.51, 123.12, 122.23, 120.54, 119.14, 109.39, 26.22 (CH₃).

P6: a yellow powder was obtained in 92% yield. $M_w = 15\ 300$ g/mol, $M_w/M_n = 1.74$. IR (KBr), ν (cm⁻¹): 3223 (N-H), 3060, 2932, 2862, 1710 (C=O), 1657 (C=O), 1606, 1580, 1488, 1469, 1375, 1341, 1247, 1157, 1090, 858, 749, 695. ¹H NMR (500 MHz, DMSO-*d*₆), δ (ppm): 12.85 (N-H), 8.01, 7.91, 7.81, 7.68, 7.46, 7.29, 7.15, 7.09, 7.01, 6.78, 6.53, 3.12 (CH₃). ¹³C NMR (125 MHz, DMSO-*d*₆), δ (ppm): 195.20 (C=O), 165.42 (NH-C=O), 159.40, 144.76, 137.70, 132.42, 131.03, 130.40, 128.52, 128.26, 126.46, 124.64, 123.03, 122.23, 118.98, 117.87, 109.38, 26.27 (CH₃).

P7 (Table S7, entry 2): a yellow powder was obtained in 90% yield. $M_w = 18\ 400$ g/mol, $M_w/M_n = 1.43$. IR (KBr), ν (cm⁻¹): 3435 (-OH), 3244 (N-H), 3063, 2928, 2858, 1714 (C=O), 1605, 1580, 1488, 1464, 1371, 1244, 1160, 1087, 873, 751, 697. ¹H NMR (500 MHz, DMSO-*d*₆), δ (ppm): 12.69 (N-H), 12.44 (N-H), 8.00, 7.67, 7.54, 7.40, 7.23, 7.11, 6.76, 6.30, 4.56 (CH), 2.02 – 1.31 (CH₂), 1.03 (CH₂), 0.82 – 0.35 (CH₂, CH₃). ¹³C

NMR (125 MHz, DMSO-*d*₆), δ (ppm): 176.93 (C=O), 175.71 (C=O), 169.46 (C=O), 166.44(C=O), 164.97 (C=O), 159.87, 151.88, 150.15, 144.67, 143.96, 143.16, 141.95, 139.86, 134.14, 131.12, 130.17, 128.71, 127.04, 123.33, 120.65, 119.26, 110.08, 108.59, 78.39 (-C-), 75.28 (-C-), 57.65 (CH), 55.88 (-C-), 55.04 (CH), 26.32 (CH₂), 22.96 (CH₂), 14.29 (CH₃).

Reversible transformation between P1' and P1. 50 mg of P1' was dissolved in 2 mL of THF. 50 μ L of concentrated hydrochloric acid was added under stirring for 20 min until the turbid solution became clear gradually. After the solution was added into 100 mL diethyl ether dropwise, precipitates were formed which were collected by filtration, which was washed by 20 mL of methanol. P1 was then obtained after the sample was dried under vacuum to a constant weight.

50 mg of P1 was dissolved in 2 mL of methanol. 15 mg LiOH was added under stirring for 20 min until the solution became clear. Then the solution was added dropwise into 100 mL diethyl ether. The precipitates were collected by filtration, which was washed by 20 mL of water and 40 mL of THF. P1' was then obtained after the sample was dried under vacuum to constant weight.

Table S1 Solvent effect on the MCP of **1a**, **2**, and **3a**^a

entry	solvent	yield (%)	M_w (g/mol) ^b	M_w/M_n ^b
1	DCM	85	6600	1.39
2	DCM/ <i>t</i> -BuOH ^c	95	11300	1.74
3	DCM/MeOH ^c	83	8700	1.34
4	THF/ <i>t</i> -BuOH ^c	74	3700	1.10
5	DMF/ <i>t</i> -BuOH ^c	23	2500	1.05
6	DMSO/ <i>t</i> -BuOH ^c	46	3600	1.09

^aCarried out at 30 °C under nitrogen for 6 h in the presence of CuI. [**1a**] = [**2**] = 0.10 M, [**3a**] = 0.25 M, [CuI] = 0.02 M, [LiOH] = 0.30 M. ^bDetermined by GPC in DMF on the basis of a PMMA calibration. ^cv/v = 10/1.

Table S2 Base effect on the MCP of **1a**, **2**, and **3a**^a

entry	base	yield (%)	M_w (g/mol) ^b	M_w/M_n ^b
1	LiOH	95	11300	1.74
2	Cs ₂ CO ₃	73	6100	1.49
3	K ₂ CO ₃	58	4500	1.12

^aCarried out at 30 °C under nitrogen for 6 h in the presence of CuI in DCM/*t*-BuOH (v/v = 10/1). [**1a**] = [**2**] = 0.10 M, [**3a**] = 0.25 M, [CuI] = 0.02 M, [base] = 0.30 M. ^bDetermined by GPC in DMF on the basis of a PMMA calibration.

Table S3 Effect of the concentration of CuI on the MCP of **1a**, **2**, and **3a**^a

entry	[CuI] (M)	yield (%)	M_w (g/mol) ^b	M_w/M_n ^b
1	0.01	89	10300	1.58
2	0.02	95	11300	1.74
3	0.03	84	10100	1.49

^aCarried out at 30 °C under nitrogen for 6 h in the presence of CuI in DCM/*t*-BuOH (v/v = 10/1). [**1a**] = [**2**] = 0.10 M, [**3a**] = 0.25 M, [LiOH] = 0.30 M. ^bDetermined by GPC in DMF on the basis of a PMMA calibration.

Table S4 Temperature effect on the MCP of **1a**, **2**, and **3a**^a

entry	T (°C)	yield (%)	M_w (g/mol) ^b	M_w/M_n ^b
1	25	87	11900	1.55
2	30	95	11300	1.74
3	35	70	6500	1.39

^aCarried out under nitrogen for 6 h in the presence of CuI in DCM/*t*-BuOH (v/v = 10/1). [**1a**] = [**2**] = 0.10 M, [**3a**] = 0.25 M, [CuI] = 0.02 M, [LiOH] = 0.30 M. ^bDetermined by GPC in DMF on the basis of a PMMA calibration.

Table S5 Monomer concentration effect on the MCP of **1a**, **2**, and **3a**^a

entry	[1a] (M)	yield (%)	M_w (g/mol) ^b	M_w/M_n ^b
1	0.05	85	12800	1.69
2	0.10	95	11300	1.74
3	0.20	94	9900	1.46
4	0.30	94	8100	1.38
5	0.40	81	7800	1.37

^aCarried out at 30 °C under nitrogen for 6 h in the presence of CuI in DCM/*t*-BuOH (v/v = 10/1). [**1a**] = [**2**], [**3a**] = 2.5[**1a**], [CuI] = 0.2 [**1a**], [LiOH] = 3 [**1a**]. ^bDetermined by GPC in DMF on the basis of a PMMA calibration.

Table S6 Effect of time on the MCP of **1a**, **2**, and **3a**^a

entry	<i>t</i> (h)	yield (%)	<i>M_w</i> (g/mol) ^b	<i>M_w</i> / <i>M_n</i> ^b
1	3	93	10100	1.32
2	6	95	11300	1.74
3	12	96	12300	1.67
4	24	98	19300	1.78

^aCarried out at 30 °C under nitrogen in the presence of CuI in DCM/*t*-BuOH (v/v = 10/1). [**1a**] = [**2**] = 0.10 M, [**3a**] = 0.25 M, [CuI] = 0.02 M, [LiOH] = 0.30 M. ^bDetermined by GPC in DMF on the basis of a PMMA calibration.

Table S7 Effect of the amount of H₂O on the MCP of **1a**, **2**, **3c**, and H₂O^a

entry	H ₂ O (eq)	yield (%)	<i>M_w</i> (g/mol) ^b	<i>M_w</i> / <i>M_n</i> ^b	[II]/[I] ^c
1	30	73	14600	1.40	32/68
2	60	90	18400	1.43	38/62
3	120	95	16300	1.52	16/84
4	180	93	17000	1.51	11/89

^aCarried out at 30 °C under nitrogen for 12 h in the presence of CuI in DMF. [**1a**] = [**2**] = 0.10 M, [**3c**] = 0.25 M, [CuI] = 0.02 M, [Na₂CO₃] = 0.30 M, [Et₄Ni] = 0.02 M. ^bDetermined by GPC in DMF on the basis of a PMMA calibration. ^cThe proportion of 3-hydroxyindole moiety (II) and 3-alkenyloxindoles moiety (I) in random copolymers.

Table S8 Effect of time on the MCP of **1a**, **2**, **3c**, and H₂O^a

entry	<i>t</i> (h)	yield (%)	<i>M_w</i> (g/mol) ^b	<i>M_w</i> / <i>M_n</i> ^b	[II]/[I] ^c
1	1	38	4200	1.14	
2	5	82	16200	1.42	39/61
3	12	90	18400	1.43	38/62
4	24	95	19800	1.46	33/67

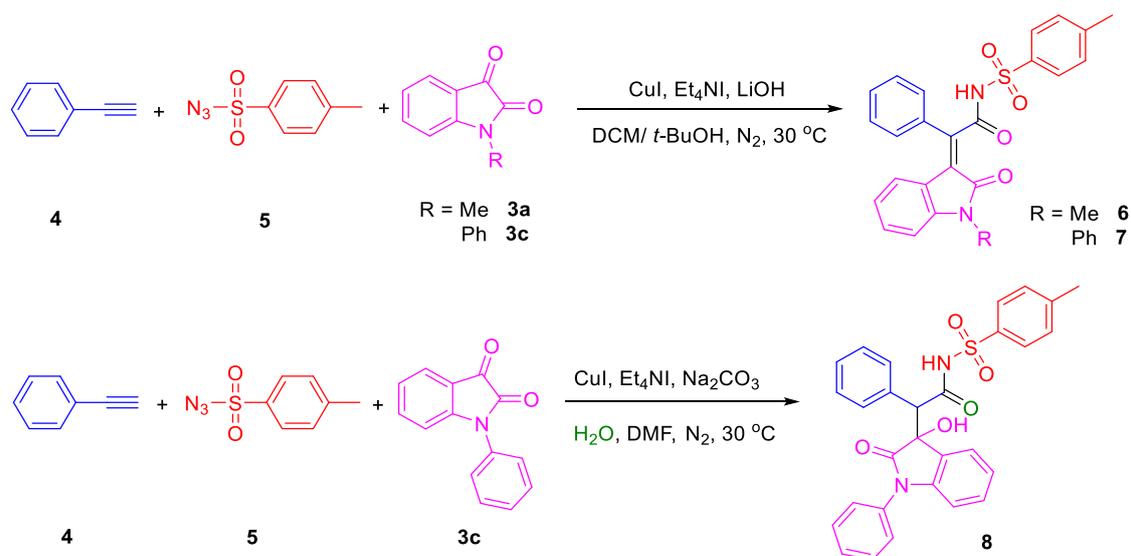
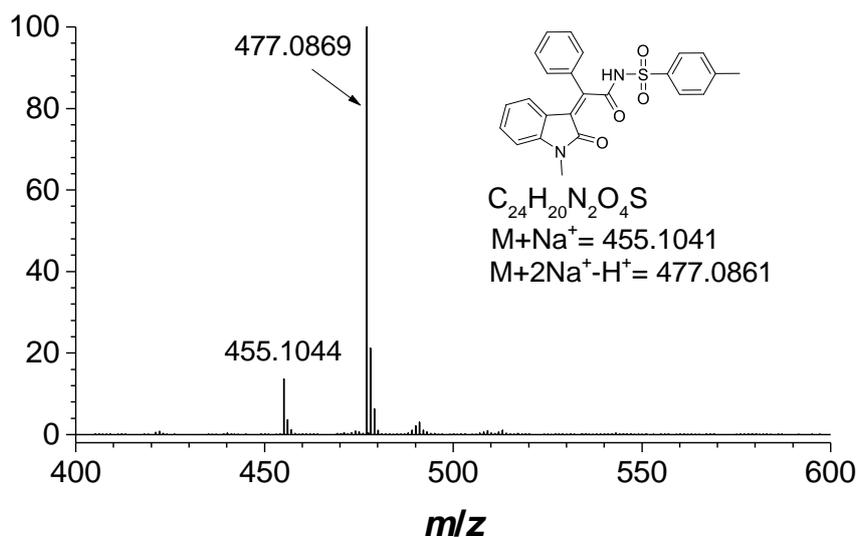
^aCarried out at 30 °C under nitrogen in the presence of CuI in DMF. [**1a**] = [**2**] = 0.10 M, [**3c**] = 0.25 M, [H₂O] = 60[**1a**], [CuI] = 0.02 M, [Na₂CO₃] = 0.30 M, [Et₄Ni] = 0.02 M. ^bDetermined by GPC in DMF on the basis of a PMMA calibration. ^cThe proportion of 3-hydroxyindole moiety (II) and 3-alkenyloxindoles moiety (I) in random copolymers.

Table S9 Monomer concentration effect on the MCP of **1a**, **2**, **3c**, and water^a

entry	[1a] (M)	yield (%)	M_w (g/mol) ^b	M_w/M_n ^b	[II]/[I] ^c
1	0.05	83	17100	1.44	47/53
2	0.10	90	18400	1.43	38/62
3	0.20	95	17700	1.53	24/76

^aCarried out at 30 °C under nitrogen for 12 h in the presence of CuI in DMF. [**1a**] = [**2**], [**3c**] = 2.5[**1a**], [H₂O] = 60[**1a**], [CuI] = 0.2 [1a], [Na₂CO₃] = 3 [1a], [Et₄Ni] = 0.2 [1a].

^bDetermined by GPC in DMF on the basis of a PMMA calibration. ^cThe proportion of 3-hydroxyindole moiety (II) and 3-alkenyloxindoles moiety (I) in random copolymers.

**Scheme S1** Synthesis of model compounds **6-8**.**Fig. S1** HR-MS spectrum of compound **6**.

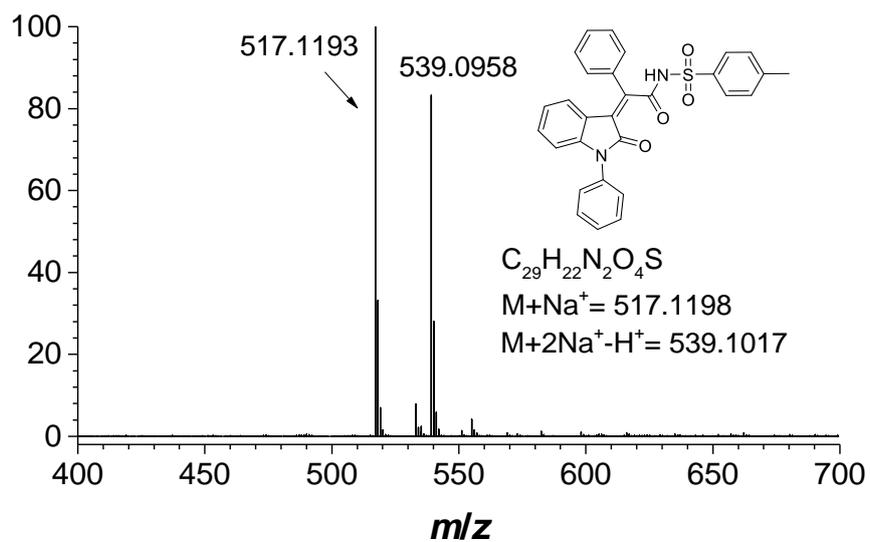


Fig. S2 HR-MS spectrum of compound 7.

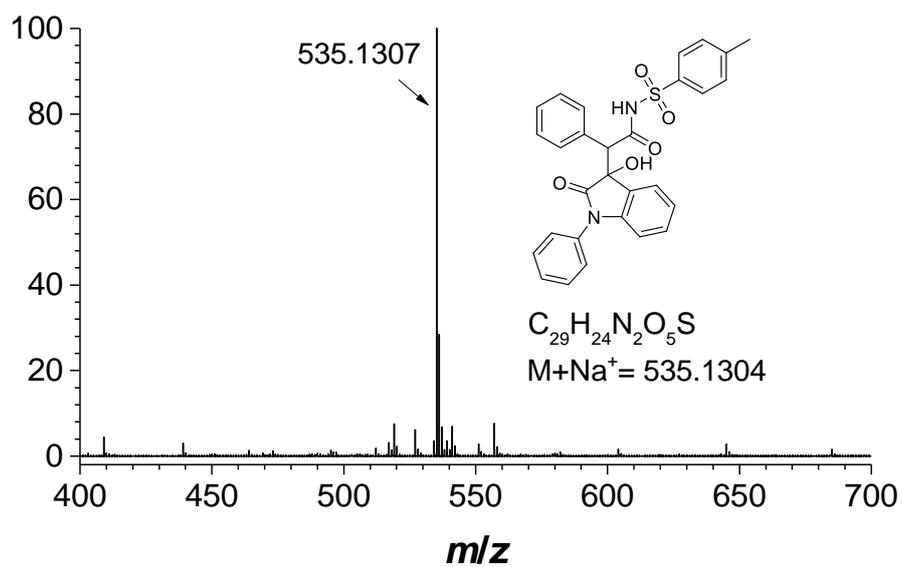


Fig. S3 HR-MS spectrum of compound 8.

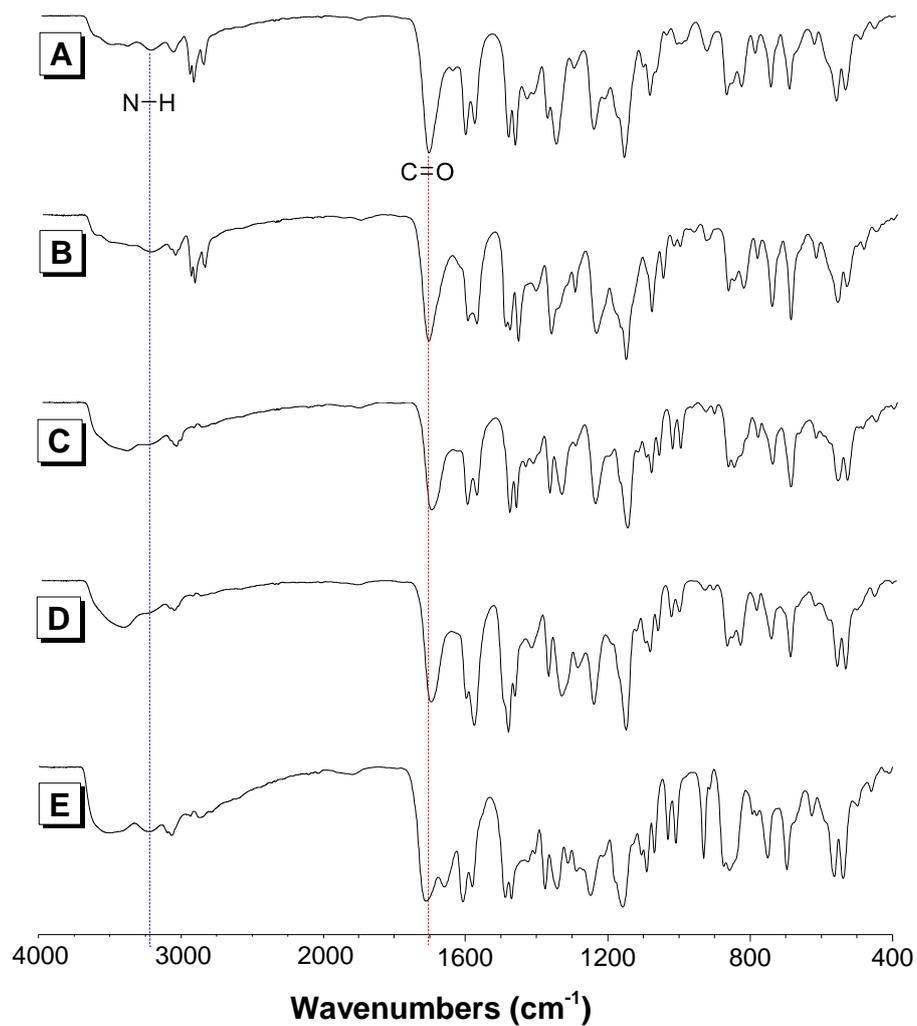


Fig. S4 IR spectra of (A) P2, (B) P3, (C) P4, (D) P5, and (E) P6.

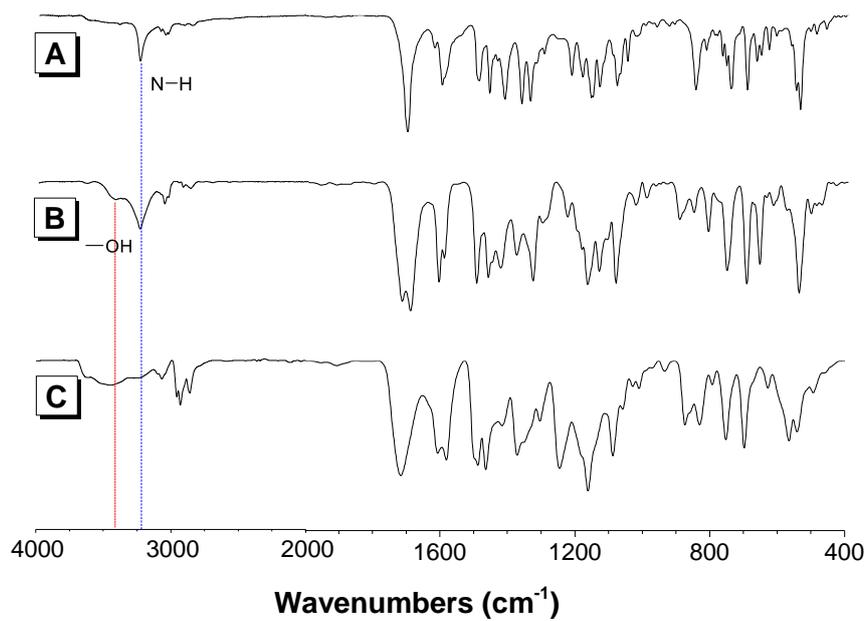


Fig. S5 IR spectra of (A) 7, (B) 8, and (C) P7.

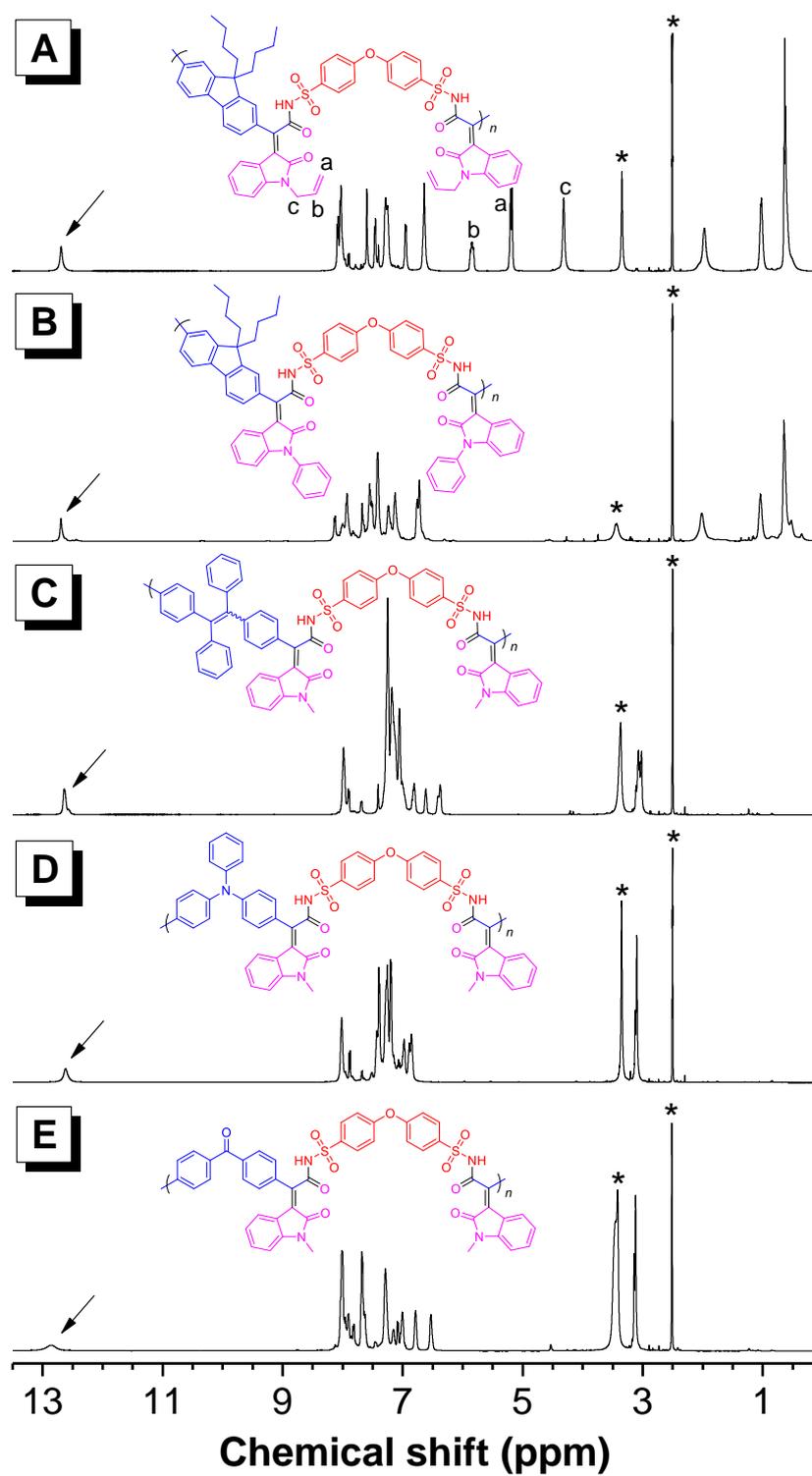


Fig. S6 ^1H NMR spectra of (A) P2, (B) P3, (C) P4, (D) P5, and (E) P6 in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

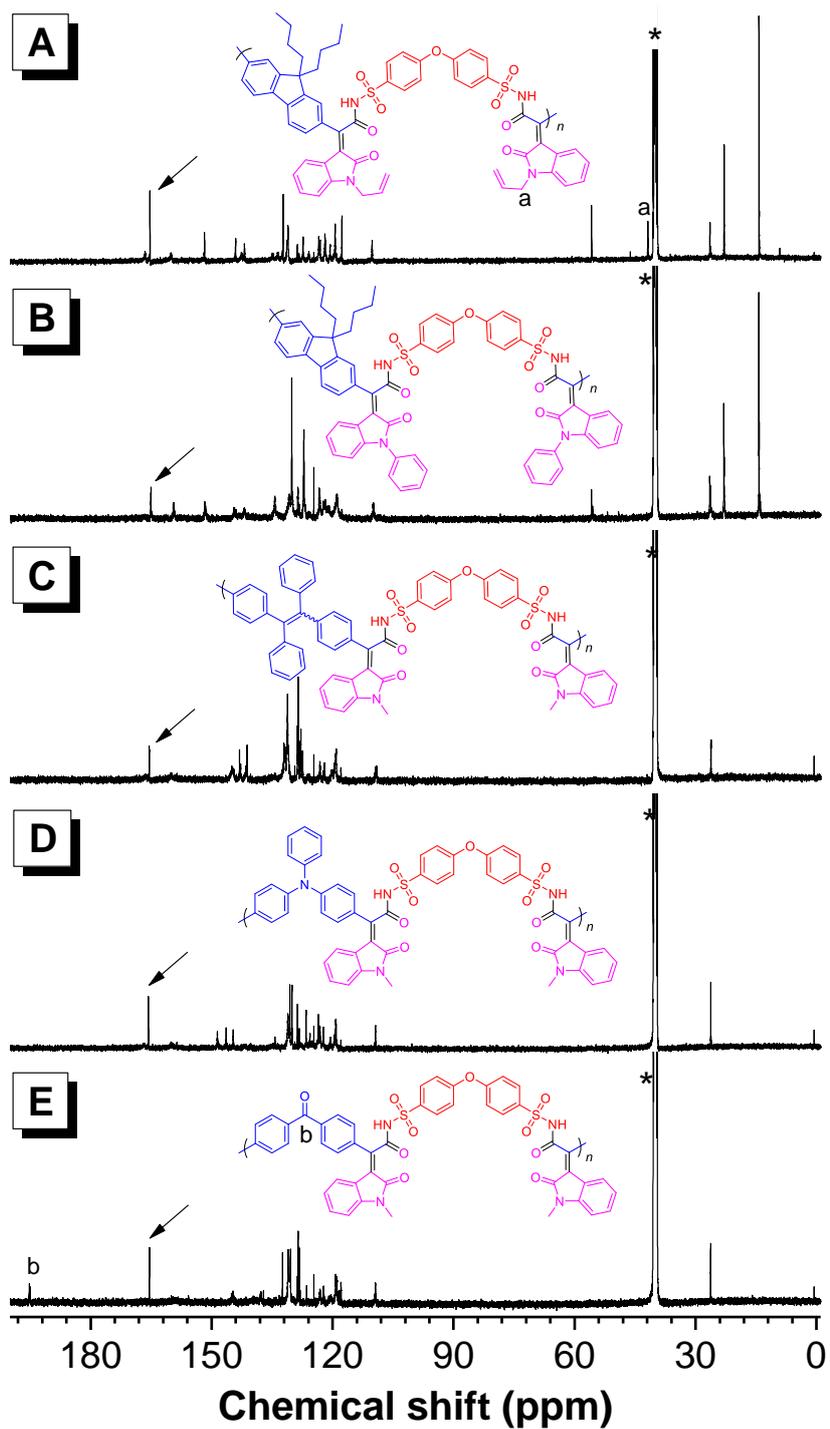


Fig. S7 ^{13}C NMR spectra of (A) P2, (B) P3, (C) P4, (D) P5, and (E) P6 in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

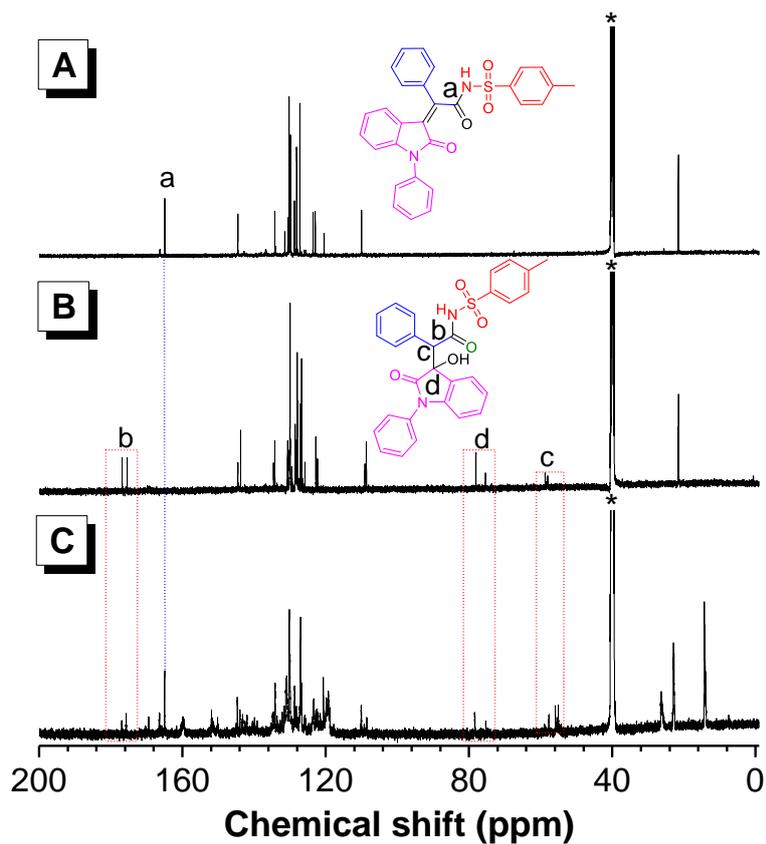


Fig. S8 ^{13}C NMR spectra of (A) **7**, (B) **8**, and (C) **P7** in $\text{DMSO-}d_6$. The solvent peaks are marked with asterisks.

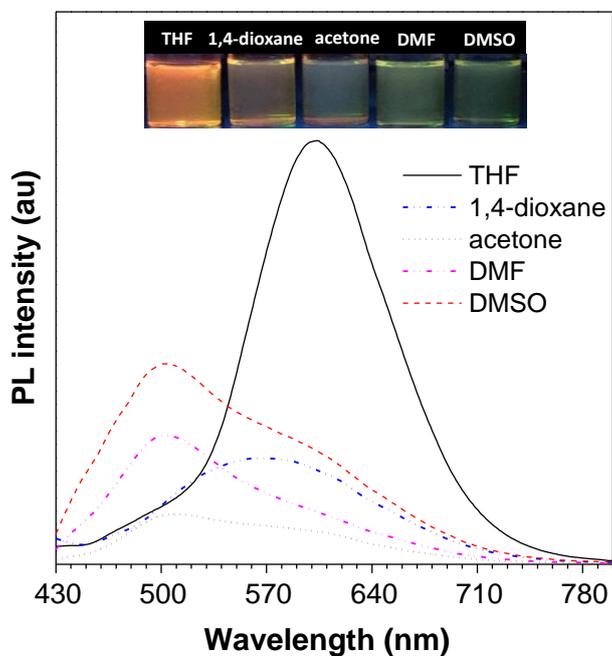


Fig. S9 PL spectra of **P5** in various solvents. Concentration: $10\ \mu\text{M}$. Excitation wavelength: $410\ \text{nm}$. Inset: fluorescent photographs of **P5** in different solvents taken under the illumination of a UV lamp ($365\ \text{nm}$).