Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Highly sensitive humidity sensor based on aggregation induced emission luminogen-appended hygroscopic polymer microresonator

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1. Materials

Unless otherwise stated, chemical reagents were purchased from Sigma-Aldrich, TCI, and Wako Pure Chemical Industries, Ltd. and used as received. Compounds **2**, **3** and **5** (Scheme S1) were prepared according to previously reported procedures[1] and unambiguously characterized by nuclear magnetic resonance (NMR), infrared (IR) and atmospheric pressure chemical ionization (APCI)-TOF mass spectrometry.

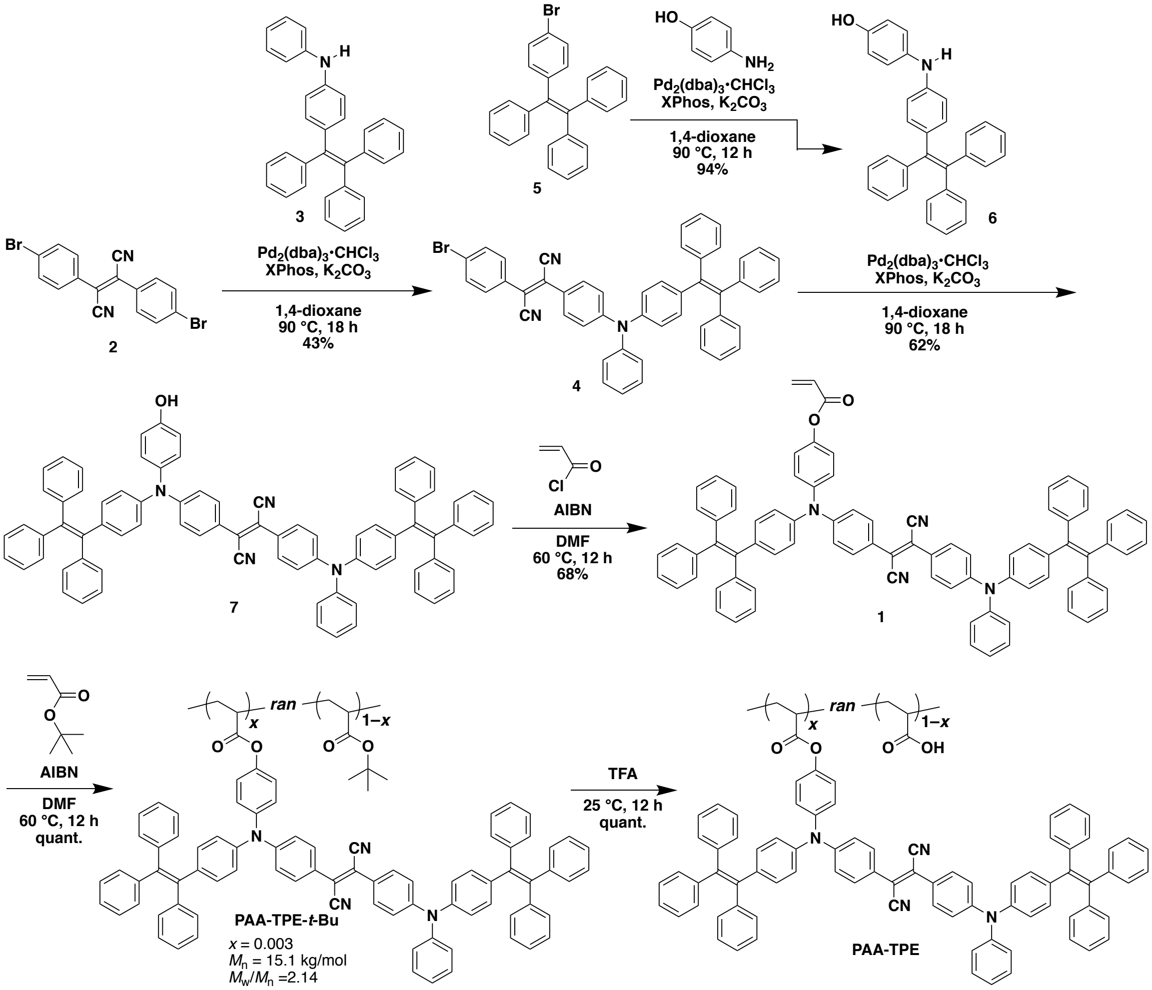
2. General

NMR spectra were recorded at 25 °C on a Bruker model AVANCE-400 spectrometer (400.0 MHz for ^{1}H and 100.6 MHz for ^{13}C), where chemical shifts (δ) were determined with respect to residual non-deuterated solvent for ^{1}H ($CDCl_3$: $^1H(\delta) = 7.26$ ppm, CD_3OD $^1H(\delta) = 3.31$ ppm), residual solvent for ^{13}C ($CDCl_3$: $^{13}C(\delta) = 78.0$ ppm). The absolute values of the coupling constants are given in Hertz (Hz), regardless of their signs. Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). IR spectra were recorded at 25 °C on a JASCO model FT/IR-660$_{Plus}$ Fourier transform infrared spectrometer. High-resolution (HR) APCI-TOF mass spectrometry measurements were performed on a Bruker microTOF II mass spectrometer equipped with an atmospheric pressure chemical ionization (APCI) probe. Analytical size-exclusion chromatography (SEC) was performed at 40 °C regulated by column oven (CO-2065$_{Plus}$) on a JASCO HSS-1500 system equipped with a refraction index (RI) detector (RI-2031$_{Plus}$) and a multiwavelength detector (MD-2010$_{Plus}$), using dimethylformamide (DMF) containing LiBr (0.01 M) as an eluent at a flow rate of 0.80 mL min^{-1} on a column (TSKgel α-3000, TOSOH). The molecular weight calibration curve was obtained by using standard polystyrenes (TSKstandard polystyrene, TOSOH).

The morphology of the **PAA-TPE** microspheres was examined by scanning electron microscopy (SEM, Hitachi model SU-8000) operating at 20 kV. Silicon was used as a substrate and Au for coating. The absorption and fluorescence spectra were measured on a UV-visible spectrometer (JASCO model UV-570) and a fluorescent spectrometer (JASCO model FP-6200), respectively. Photoluminescence quantum yield was recorded on a Hamamatsu model C9920–02 absolute PL quantum yield measurement system. Optical and fluorescent microscopic images were taken from Olympus model BX53 Upright Microscope. Refractive index was measured by ellipsometry (J. A. Woollam Japan model M-2000).

3. Synthesis of PAA-TPE

Scheme S1. Synthesis of **PAA-TPE**.



4: Under Ar, a 1,4-dioxane solution (20 mL) of a mixture of 2,3-bis(4-bromophenyl)fumaronitrile (**2**)[1] (100 mg, 0.260 mmol), *N*-(4-(1,2,2-triphenylvinyl)phenyl)benzenamine (**3**)[1] (80.0 mg, 0.190 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 10.0 mg, 20.0 μmol), $Pd_2(dba)_3$•$CHCl_3$ (6.00 mg, 5.16 μmol) and K_2CO_3 (66.0 mg, 0.480 mmol) was stirred at 90 °C for 18 h. After allowed to cool to 25 °C, the reaction mixture was evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$ (100 mL), washed with brine, dried over anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on SiO_2 (hexane/$CHCl_3$; v/v = 7/1) to allow isolation of **4** as a red solid (81.5 mg, 112 μmol) in 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 7.36 (d, 2H, J = 8.4 Hz), 6.87 (s, 2H), 6.79–6.59 (m, 26H), 6.51 (d, 2H, J = 8.4) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 293K) δ 116.6, 117.4, 118.6, 118.8, 123.3, 125.0, 125.6, 126.1, 126.2, 126.5, 126.6, 127.6, 127.7, 127.7, 127.8, 128.7, 128.9, 130.2, 130.6, 130.7, 131.3, 131.4, 131.8, 132.4, 132.6, 140.3, 140.7, 141.4, 143.2, 143.4, 143.8, 144.1, 145.8, 151.1 ppm. FT-IR (KBr) ν 3448, 3076, 3056, 3023, 2963, 2928, 2854, 2215, 1591, 1544, 1506, 1443, 1397, 1331, 1294, 1262, 1200, 1156, 1110, 1076, 1029, 1010, 916, 849, 824, 754, 699, 636, 615 cm^{-1}. HR-MS (APCI) calcd for $C_{48}H_{32}Br_1N_3$ [M$^+$] 729.1774, found 729.1763. Analytical data (^{1}H and ^{13}C NMR, FT-IR, and high-resolution APCI-TOF mass spectra) of **4** are shown in Figs. S1–S4.

6: Under Ar, a 1,4-dioxane solution (10 mL) of a mixture of 4-(1,2,2-triphenylvinyl)phenyl bromide (**5**)[1] (1.00 g, 2.43 mmol) and 4-aminophenol (531 mg, 4.86 mmol), XPhos, (93.0 mg, 0.190 mmol), $Pd_2(dba)_3$•$CHCl_3$ (50.0 mg, 50.0 µmol) and K_2CO_3 (0.620 g, 4.52 mmol) was stirred at 90 °C for 12 h. After allowed to cool to 25 °C, the reaction mixture was evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$ (200 mL), washed with brine, dried over anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on SiO_2 ($CHCl_3$) to allow isolation of **6** as a yellow powder (1.00 g, 2.28 mmol) in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 7.18–6.99 (m, 15H), 6.97 (d, 2H, J = 8.6 Hz), 6.86 (d, 2H, J = 8.48 Hz), 6.75 (d, 2H, J = 8.6 Hz), 6.64 (d, 2H, J = 8.84 Hz), 5.44 (s, 1H), 4.68 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 293K) δ 114.5, 116.1, 122.3, 126.1, 126.2, 126.3, 127.6, 127.7, 131.1, 131.4, 131.4, 132.5, 135.0, 135.6, 139.6, 140.9, 143.4, 144.1, 144.2, 144.3, 151.0 ppm. FT-IR (KBr) ν 3403, 3076, 3055, 3024, 2965, 2923, 2364, 2345, 1607, 1510, 1442, 1396, 1318, 1257, 1227, 1182, 1102, 1075, 1030, 915, 878, 821, 764, 751, 730, 700, 616, 583, 571 cm^{-1}. HR-MS (APCI) calcd for $C_{32}H_{25}NO$ [M$^+$] 439.1931, found 439.1959. Analytical data (^{1}H and ^{13}C NMR, FT-IR, and high-resolution APCI-TOF mass spectra) of **6** are shown in Figs. S5–S8.

7: Under Ar, a 1,4-dioxane solution (2.0 mL) of **4** (29.0 mg, 40.0 µmol), **6** (35.0 mg, 80.0 µmol), XPhos (3.00 mg, 6.29 µmol), $Pd_2(dba)_3$•$CHCl_3$ (2.00 mg, 1.93 µmol) and K_2CO_3 (11.0 mg, 80.0 µmol) was stirred at 90 °C for 18 h. After allowed to cool to 25 °C, the reaction mixture was evaporated to dryness under reduced pressure. The residue was dissolved in $CHCl_3$ (100 mL), washed with brine, dried over anhydrous $MgSO_4$ and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on SiO_2 (hexane/$CHCl_3$; v/v = 5/1) to allow isolation of **7** as a red solid (27 mg, 24.8 mmol) in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ 7.72 (dd, 4H, J = 16.8 Hz), 7.32 (t, 2H, J = 8.8 Hz), 7.18–6.85 (m, 42H), 6.79 (d, 4H, J = 12 Hz), 5.64 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 293K) δ 116.2, 117.1, 117.4, 118.8, 120.1, 120.2, 121.4, 121.6, 123.4, 124.8, 124.8, 125.8, 125.8, 126.2, 126.2, 126.3, 126.4, 126.4, 126.5, 126.6, 127.5, 127.6, 127.6, 127.6, 127.7, 127.7, 127.8, 128.6, 128.8, 130.5, 131.3, 131.3, 31.3, 131.4, 132.5, 132.5, 136.3, 138.8, 140.0, 140.3, 140.4, 140.6, 141.3, 141.6, 143.2, 143.4, 143.8, 143.8, 144.0, 144.1, 144.2, 146.0, 148.1, 150.6 ppm. FT-IR (KBr) ν 3449, 3078, 3054, 3027, 2963, 2925, 2853, 2213, 1594, 1499, 1443, 1329, 1292, 1247, 1201, 1173, 1101, 1074, 1028, 872, 823, 762, 751, 698, 627 cm^{-1}. HR-MS (APCI) calcd for $C_{80}H_{56}N_4O$ [M$^+$] 1088.4449, found 1088.4435. Analytical data (^{1}H and ^{13}C NMR, FT-IR, and high-resolution APCI-TOF mass spectra) of **7** are shown in Figs. S9–S12.

1: Acryloyl chloride (22.6 µL, 0.280 mmol) was dropwise added at 0 °C to a CH_2Cl_2 solution (2 mL) of a mixture of **7** (151 mg, 0.139 mmol) and triethylamine (78.1 µL, 0.560 mmol). The resulting mixture was stirred at 25 °C for 12 h and evaporated to dryness under reduced pressure. The residue was subjected to column chromatography on SiO_2 ($CHCl_3$) to allow isolation of **7** as a red solid (108 mg, 94 µmol) in 68% yield. ^{1}H NMR

(400 MHz, CDCl$_3$, 293 K) δ 7.74 (dd, 4H, J = 8.8, 23.7 Hz), 7.32 (t, 2H, J = 7.8 Hz), 7.22 (d, 2H, J = 8.8 Hz), 7.18–7.00 (m, 41H), 6.97 (dd, 4H, J = 2.2, 8.6 Hz), 6.89 (d, 2H, J = 8.6 Hz), 6.46 (dd, 1H, J = 1.8, 16.7 Hz), 6.14 (dd, 21H, J = 10.3, 16.7 Hz), 5.65 (dd, 1H, J = 1.8, 10.3 Hz) ppm. ^{13}C NMR (100 MHz, CDCl$_3$, 293K) δ 116.6, 117.0, 117.6, 117.6, 118.4, 118.7, 120.2, 120.2, 120.3, 123.7, 124.1, 124.8, 124.8, 125.8, 126.4, 126.5, 126.5, 126.6, 126.6, 126.7, 126.8, 127.4, 127.4, 127.5, 127.6, 127.6, 127.7, 127.7, 127.8, 128.4, 128.3, 128.5, 128.6, 128.8, 130.6, 130.6, 131.1, 131.2, 31.2, 131.3, 131.3, 131.3, 131.3, 132.2, 132.6, 138.7, 138.8, 140.3, 140.5, 141.3, 143.0, 143.2, 143.4, 143.8, 144.2, 146.0, 150.7 ppm. FT-IR (KBr) ν 3434, 3103, 3075, 3055, 3029, 2969, 2925, 2855, 2218, 1947, 1072, 1593, 1500, 1443, 1401, 1329, 1294, 1243, 1202, 1174, 1106, 1075, 1029, 1016, 981, 871, 849, 832, 753, 699 cm^{-1}. HR-MS (APCI) calcd for $C_{83}H_{58}N_4O_2$ [M$^+$] 1142.4554, found 1142.4520. Analytical data (^{1}H and ^{13}C NMR, FT-IR, and high-resolution APCI-TOF mass spectra) of **1** are shown in Figs. S13–S16.

PAA-TPE-*t*-Bu: An anisole solution (1.27 mL) of a mixture of **1** (2.0 mg, 0.00175 mmol), *t*-butyl acrylate (85 μL, 583 μmol) and AIBN (0.96 mg, 5.85 μmol) was degassed by freeze-pump-thaw cycles (three times) and purged with argon. The mixture was stirred at 65 °C for 24 h, allowed to cool to 25 °C and then evaporated to dryness under reduced pressure. The residue was purified by recycling preparative SEC (THF) to allow isolation of **PAA-TPE-*t*-Bu** as an orange solid. (156.8 mg, 69%). The composition ratio (x = 0.003) was confirmed by UV-vis absorption spectroscopy: ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 2.18–2.36 (br), 1.17–1.90 (br). FT-IR (KBr) ν (cm^{-1}) 2978, 2935, 1730, 1480, 1455, 1393, 1368, 1257, 1149, 1038, 909, 845. M_n = 15.1 kg mol^{-1}, PDI = 2.14 (SEC; based on polystyrene standards). Analytical data (^{1}H and FT-IR spectra and SEC trace) of **PAA-TPE-*t*-Bu** are shown in Figs. S17–S19.

PAA-TPE: A trifluoroacetic acid (1.3 mL) was added to **PAA-TPE-*t*-Bu** (30 mg). The mixture was stirred at 25 °C for 18 h and evaporated to dryness under reduced pressure. The residual volatile compounds were azeotropically removed with methanol (10 mL, five times) to afford **PAA-TPE** quantitatively as an orange solid (18 mg): ^{1}H NMR (400 MHz, CD$_3$OD) δ (ppm) 2.41–2.54 (br), 1.23–2.08 (br). FT-IR (KBr) ν (cm^{-1}) 3127, 1707, 1452, 1407, 1247, 1174, 1034, 804. Analytical data (^{1}H and FT-IR spectra) of **PAA-TPE** are shown in Figs. S20 and S21.

4. Analytical data

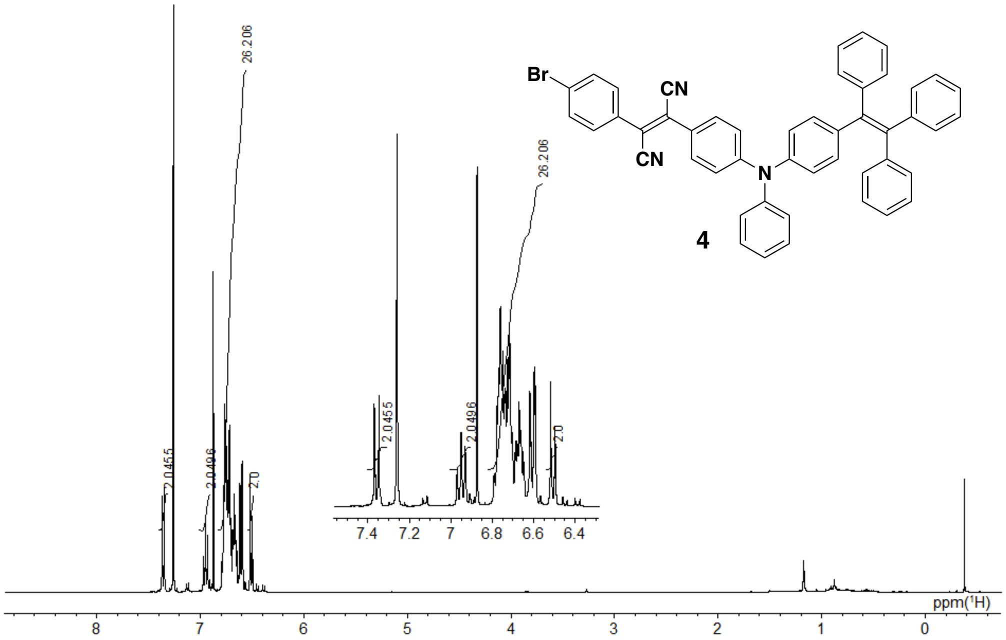


Fig. S1. ^{1}H NMR spectrum (400 MHz) of **4** in $CDCl_3$ at 25 °C.

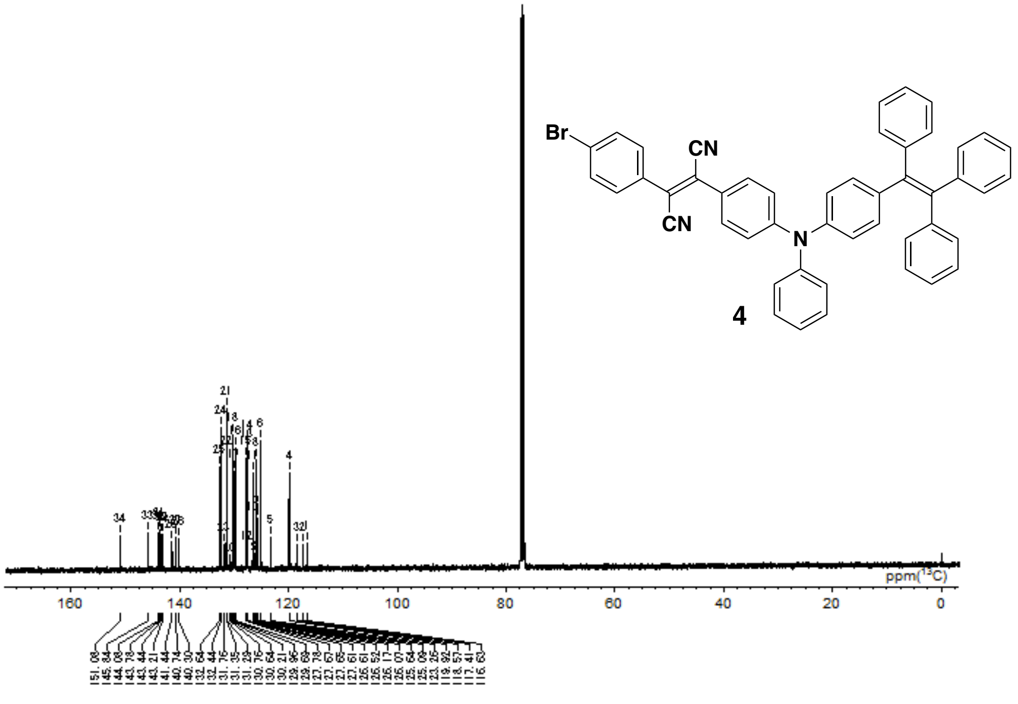


Fig. S2. ^{13}C NMR spectrum (100 MHz) of **4** in $CDCl_3$ at 25 °C.

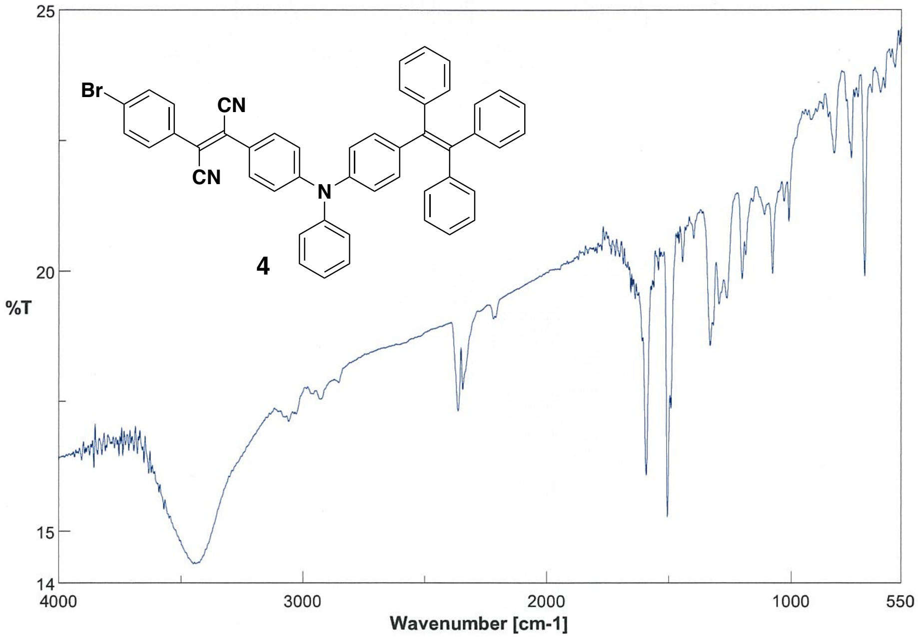


Fig. S3. FT-IR spectrum of **4** at 25 °C (KBr).

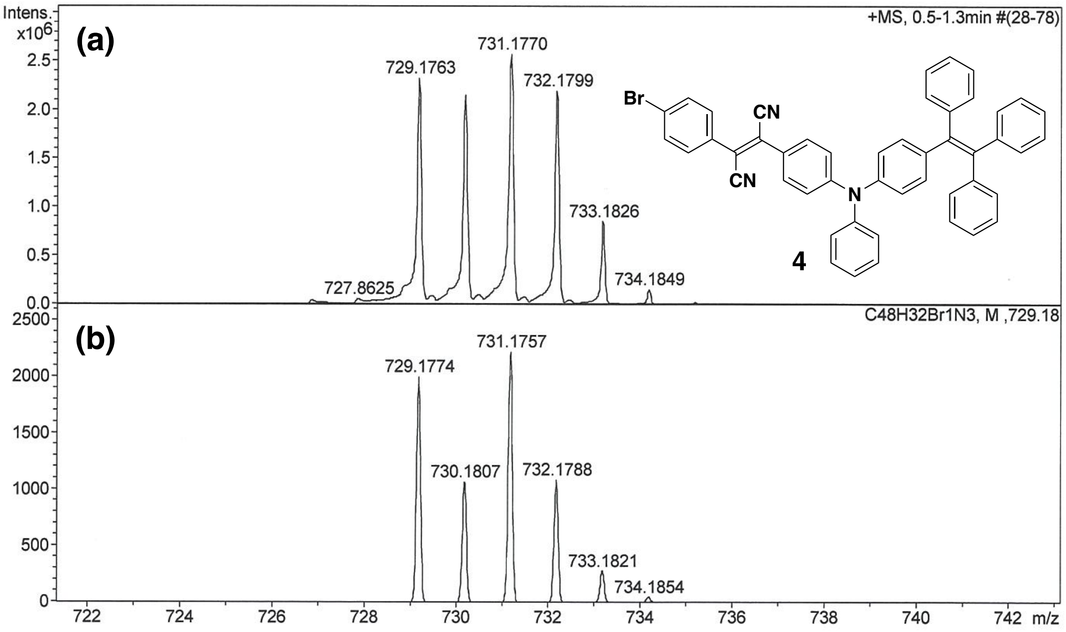


Fig. S4. (a) Observed and (b) simulated for $[M]^+$ high-resolution APCI mass spectra of **4**.

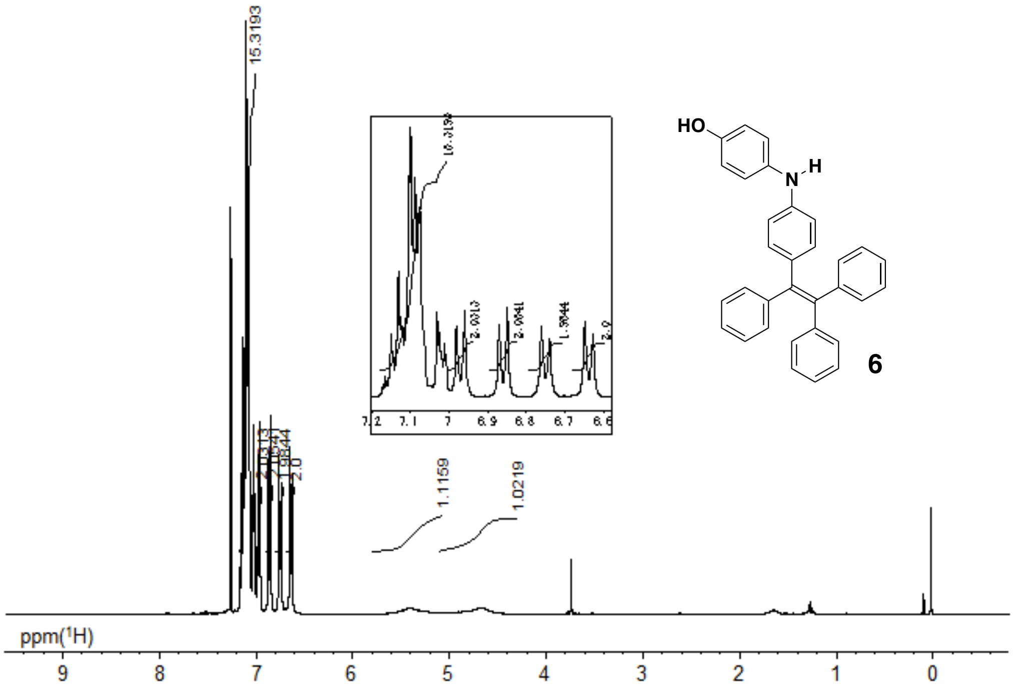


Fig. S5. ^{1}H NMR spectrum (400 MHz) of **6** in CDCl$_3$ at 25 °C.

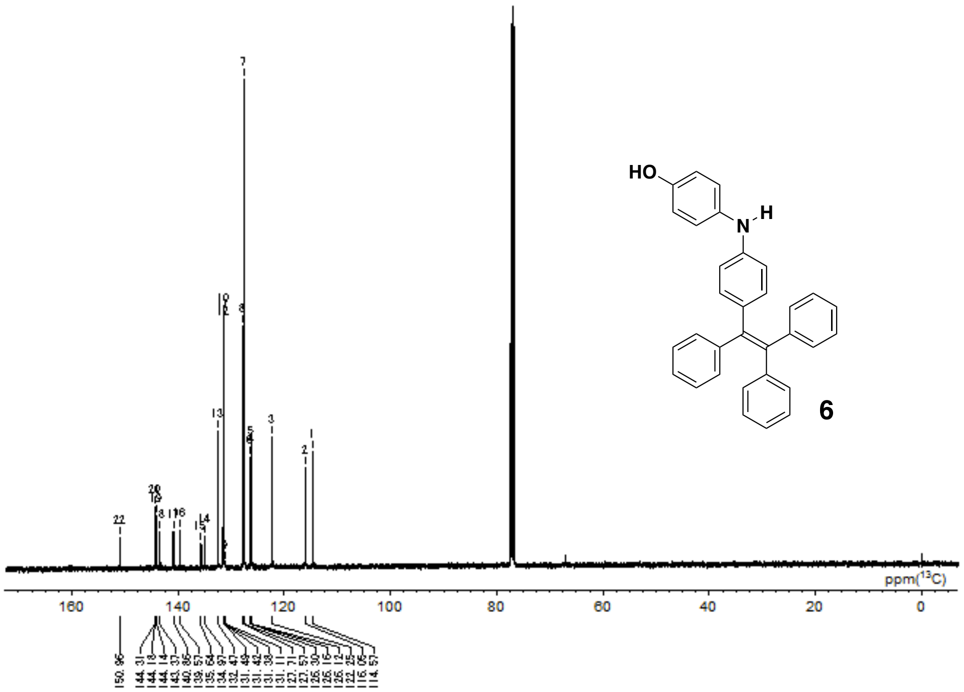


Fig. S6. ^{13}C NMR spectrum (100 MHz) of **6** in CDCl$_3$ at 25 °C.

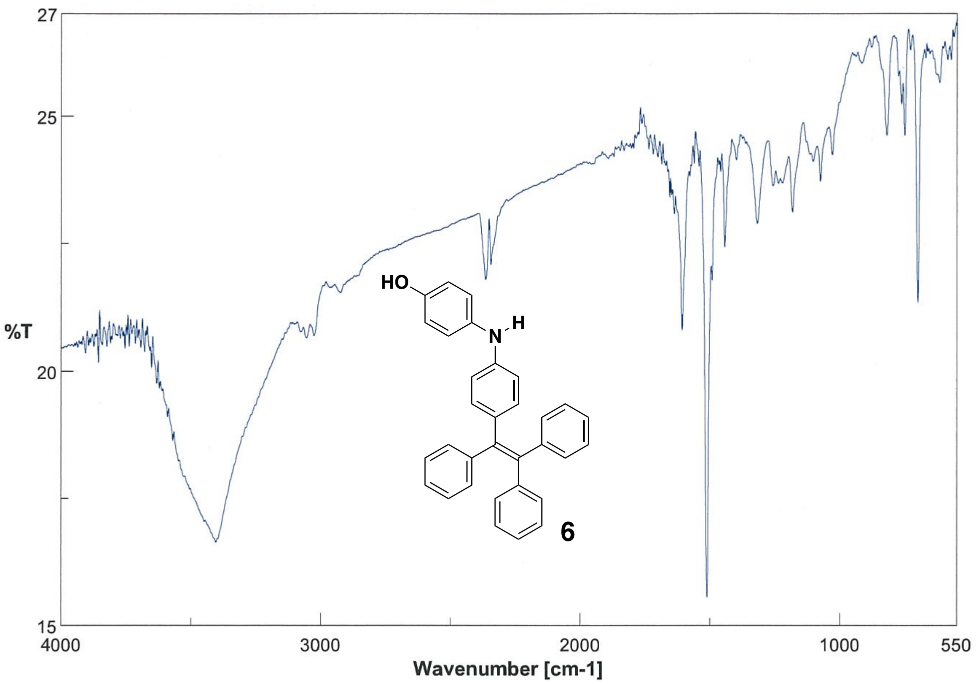


Fig. S7. FT-IR spectrum of **6** at 25 °C (KBr).

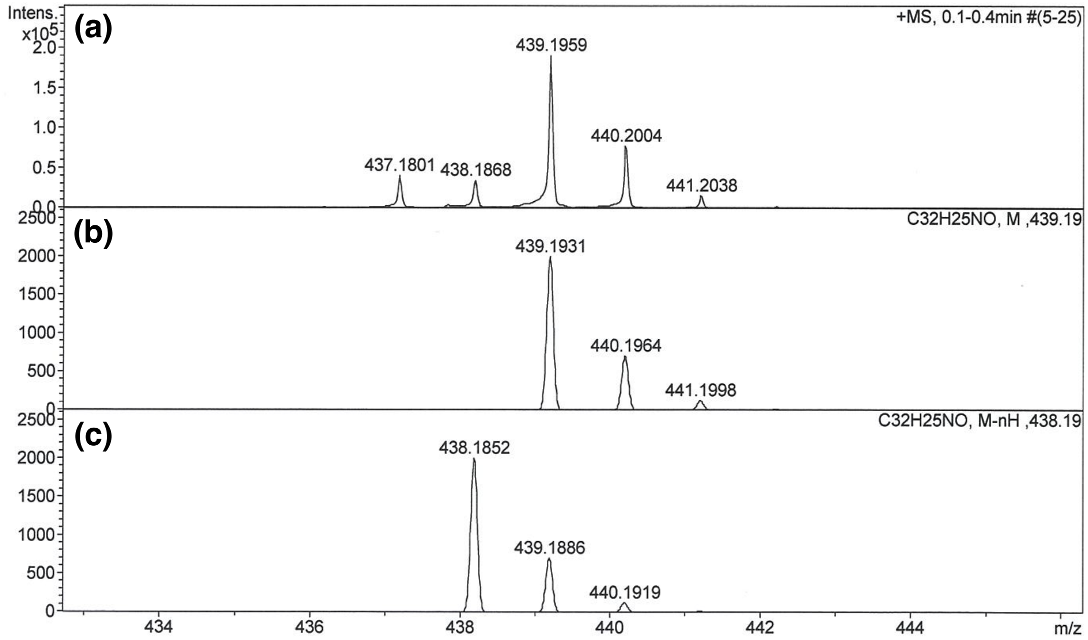


Fig. S8. (a) Observed and simulated (b for [M]+, c for [M–H]+) high-resolution APCI mass spectra of **6**.

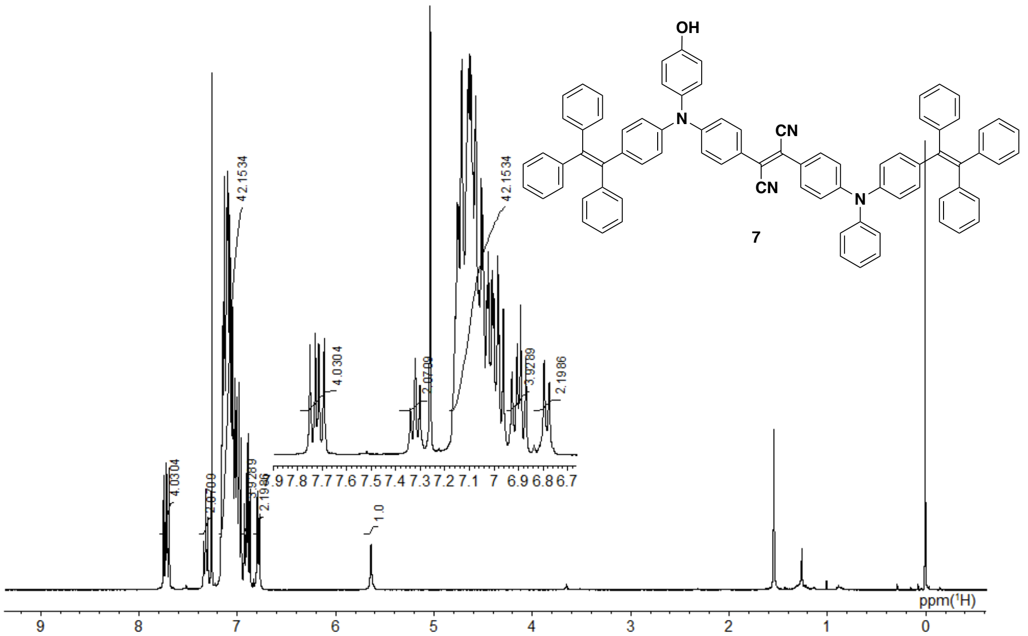


Fig. S9. ^{1}H NMR spectrum (400 MHz) of **7** in CDCl$_3$ at 25 °C.

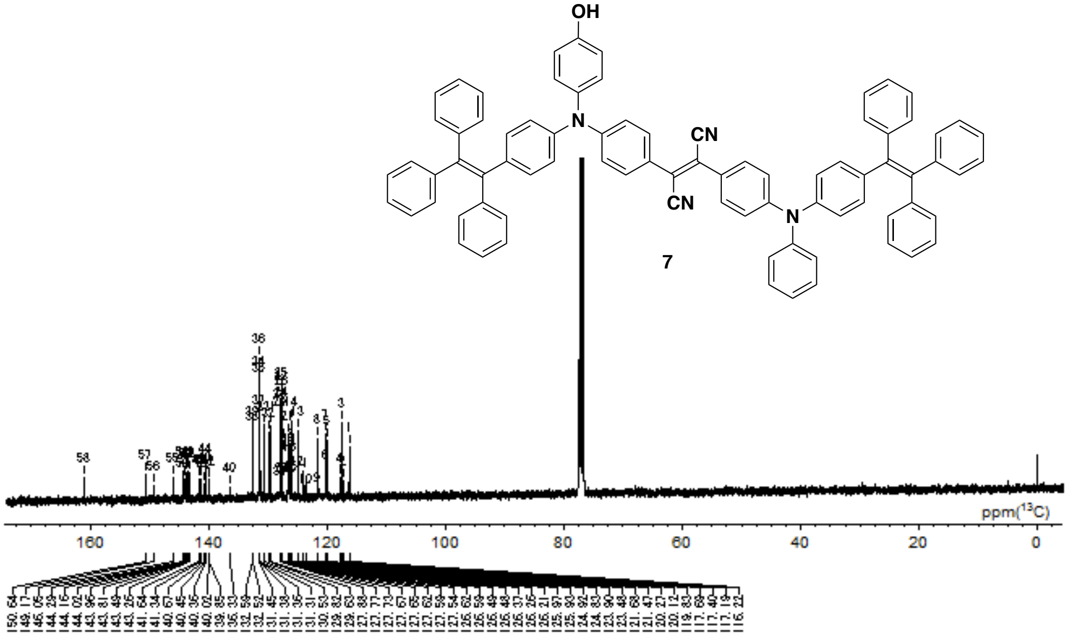


Fig. S10. ^{13}C NMR spectrum (100 MHz) of **7** in CDCl$_3$ at 25 °C.

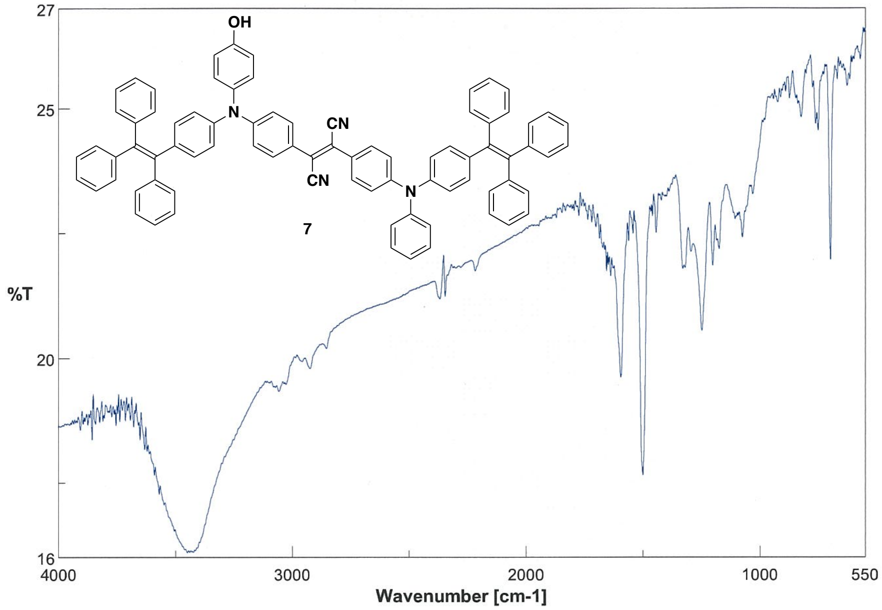


Fig. S11. FT-IR spectrum of **7** at 25 °C (KBr).

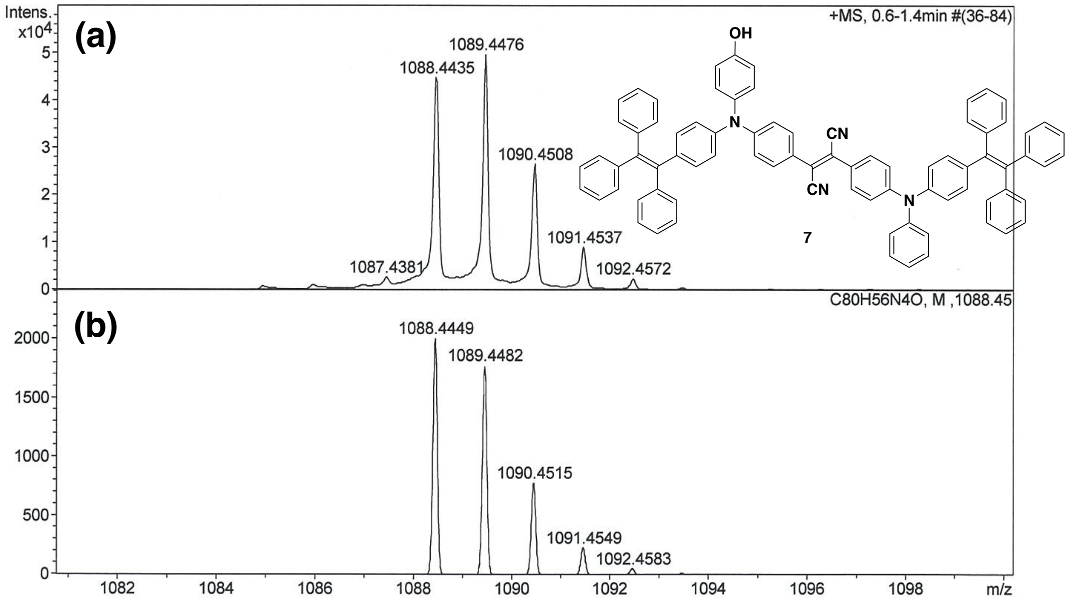


Fig. S12. (a) Observed and (b) simulated for $[M]^+$ high-resolution APCI mass spectra of **7**.

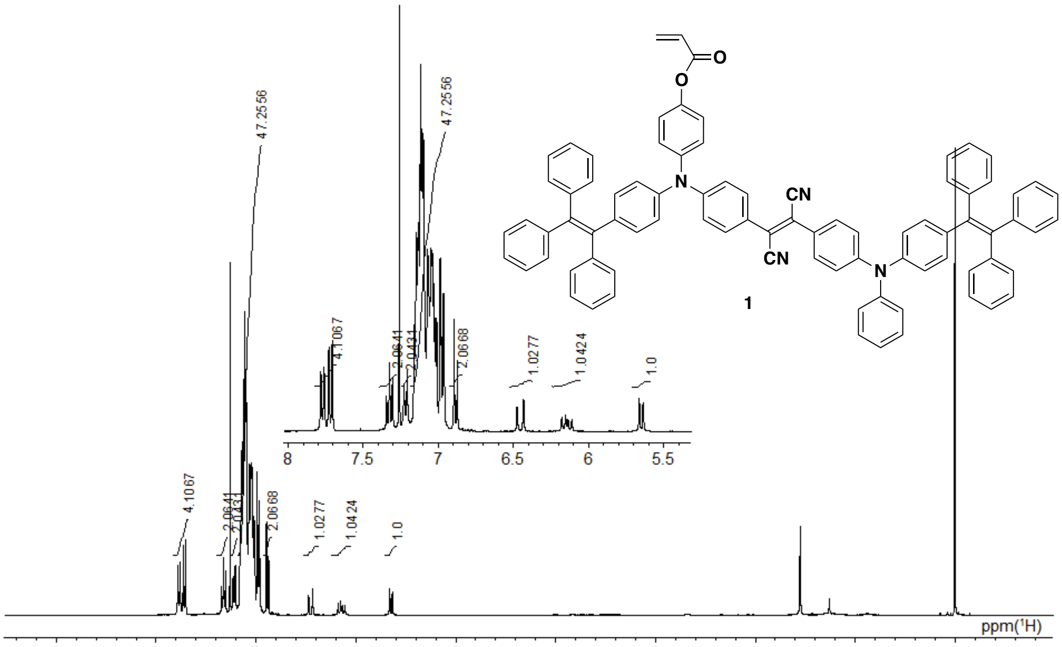


Fig. S13. ^{1}H NMR spectrum (400 MHz) of **1** in CDCl$_3$ at 25 °C.

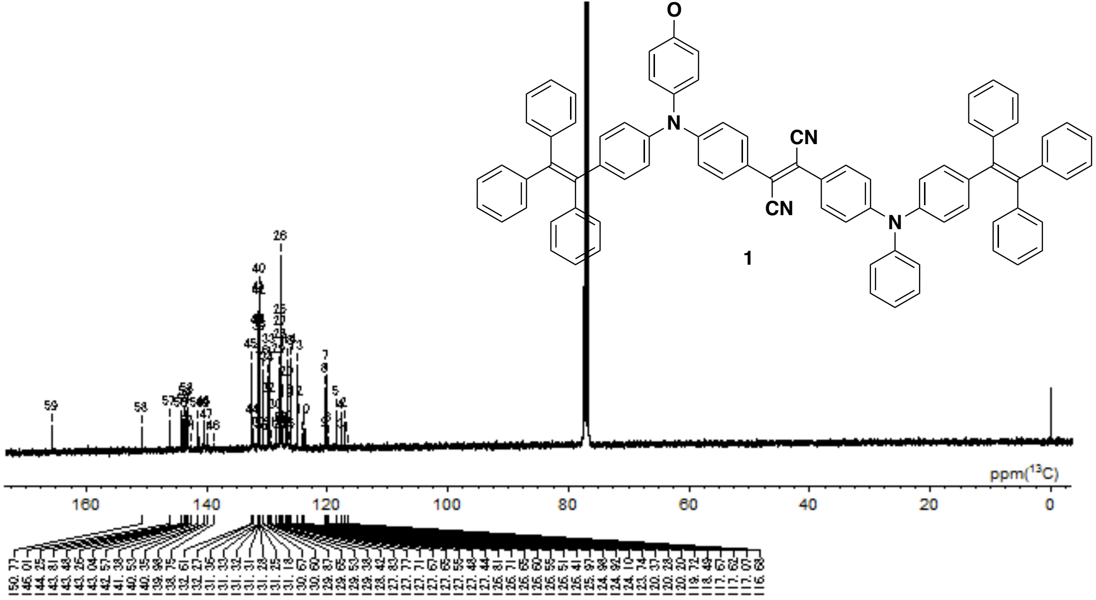


Fig. S14. ^{13}C NMR spectrum (100 MHz) of **1** in CDCl$_3$ at 25 °C.

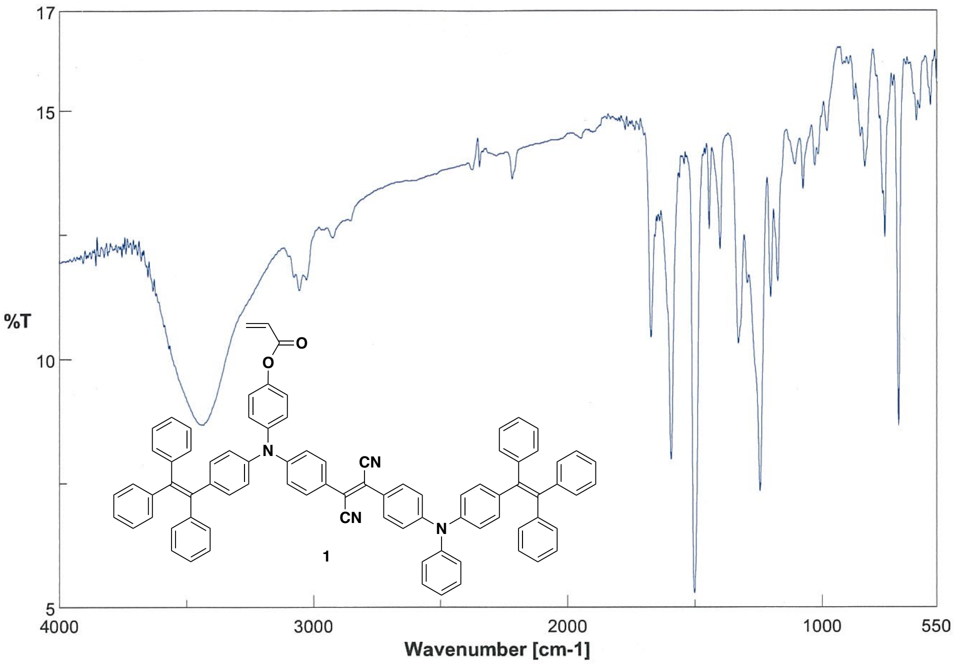


Fig. S15. FT-IR spectrum of **1** at 25 °C (KBr).

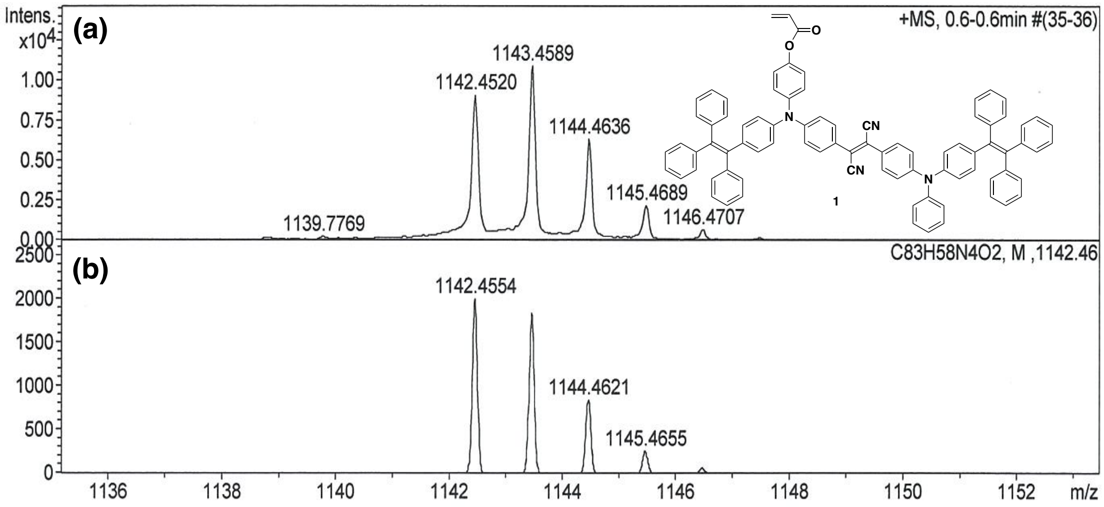


Fig. S16. (a) Observed and (b) simulated for $[\mathrm{M}]^+$ high-resolution APCI mass spectra of **1**.

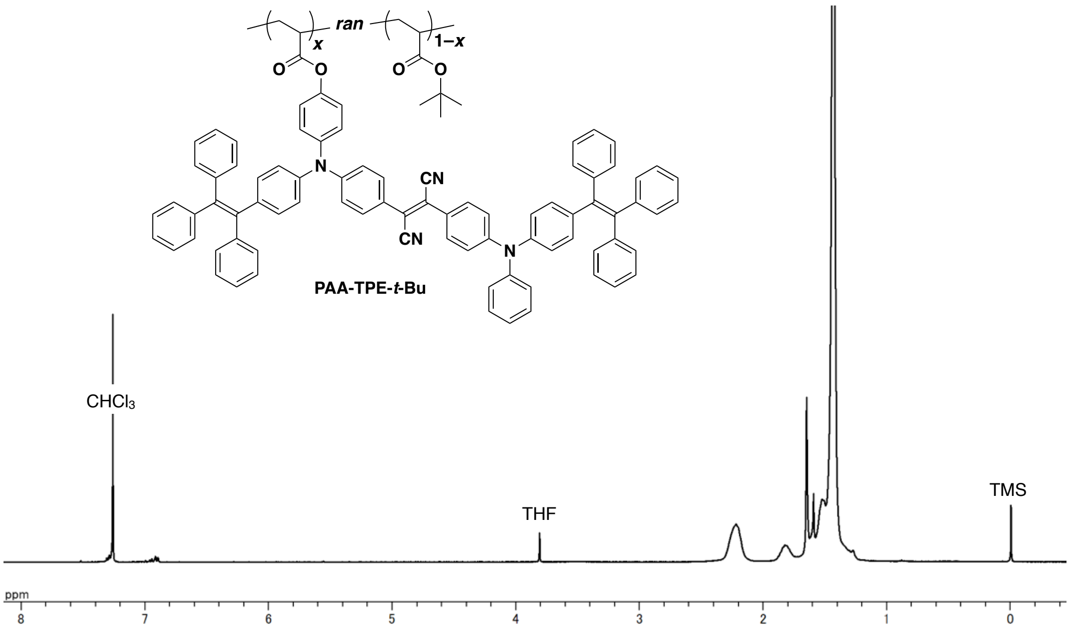


Fig. S17. ^{1}H NMR spectrum of **PAA-TPE-*t*-Bu** (400 MHz) in $CDCl_3$ at 25 °C.

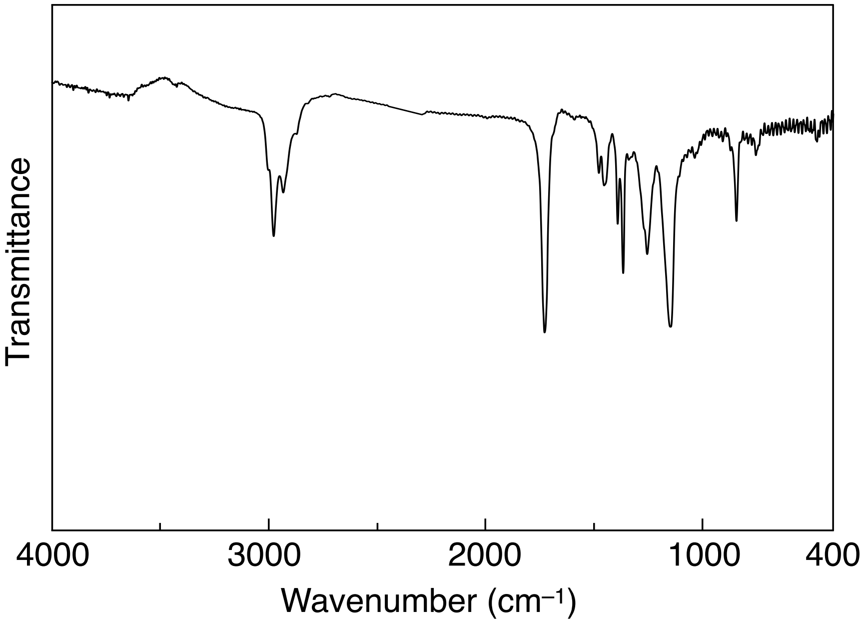


Fig. S18. IR spectrum of **PAA-TPE-*t*-Bu** at 25 °C (KBr).

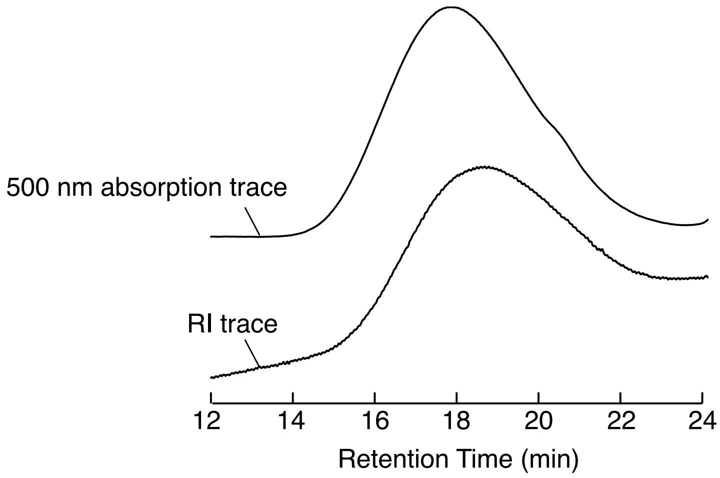


Fig. S19. SEC traces of **PAA-TPE-*t*-Bu** (eluent; DMF with 0.01 M of LiBr).

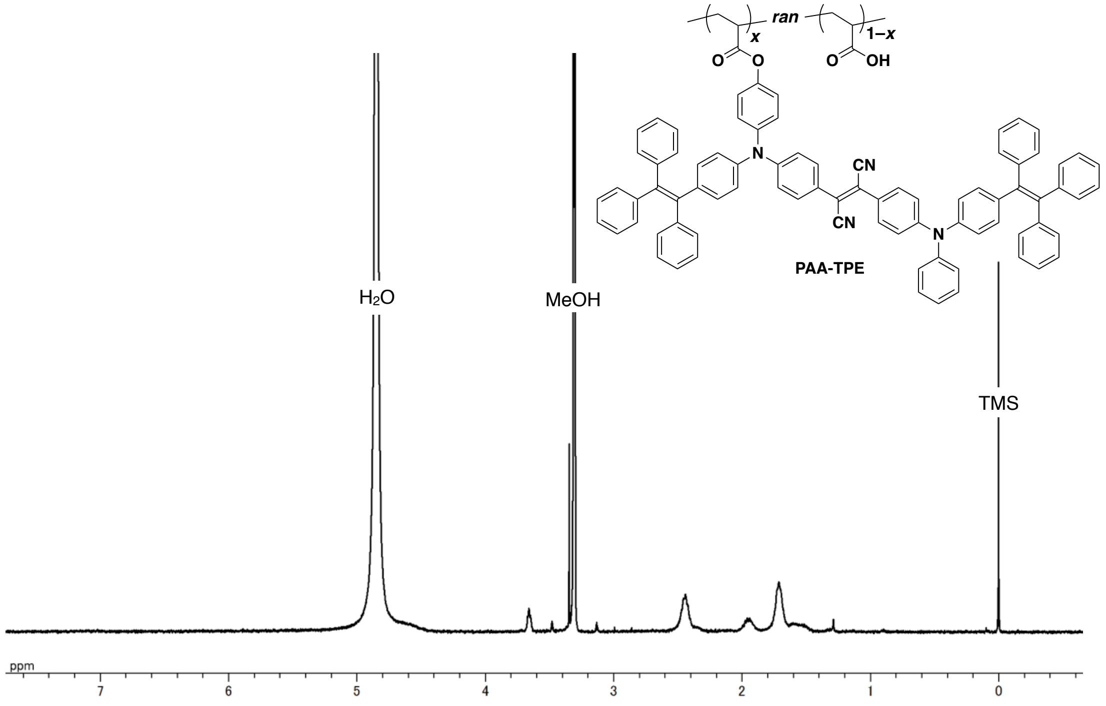


Fig. S20. ^{1}H NMR spectrum of **PAA-TPE** (400 MHz) in CD_3OD at 25 °C.

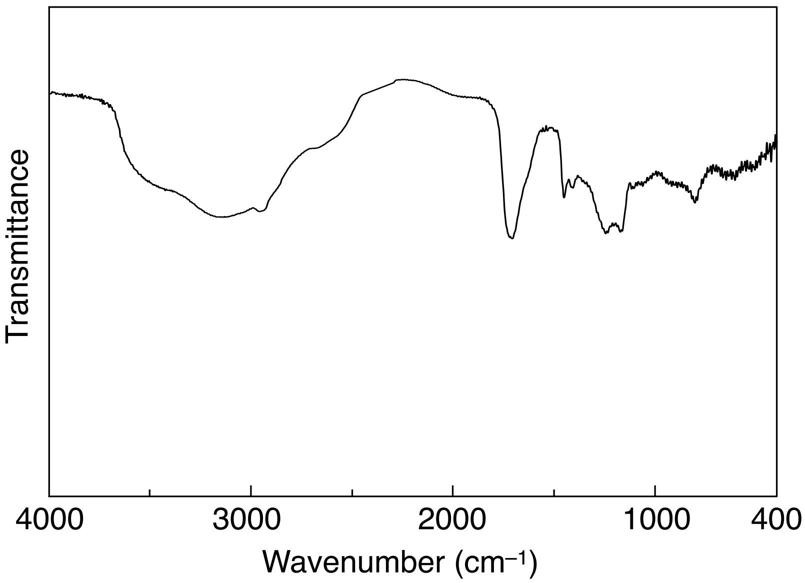


Fig. S21. IR spectrum of **PAA-TPE** at 25 °C (KBr).

5. Preparation of PAA-TPE microspheres

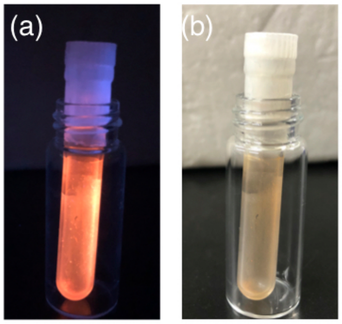


Fig. S22. Photographic images of **PAA-TPE** microspheres in a glass tube after the interphase precipitation taken under illumination of UV light (a) and white light (b).

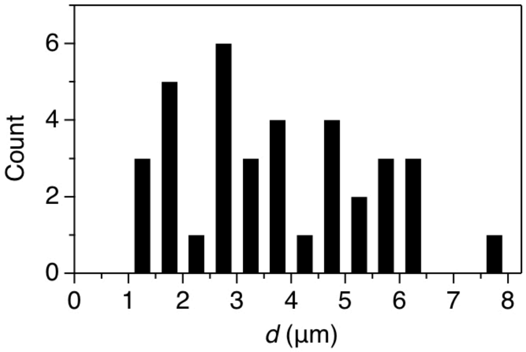


Fig. S23. Histogram of the diameter of the microspheres of **PAA-TPE**.

6. *μ*-PL spectroscopy

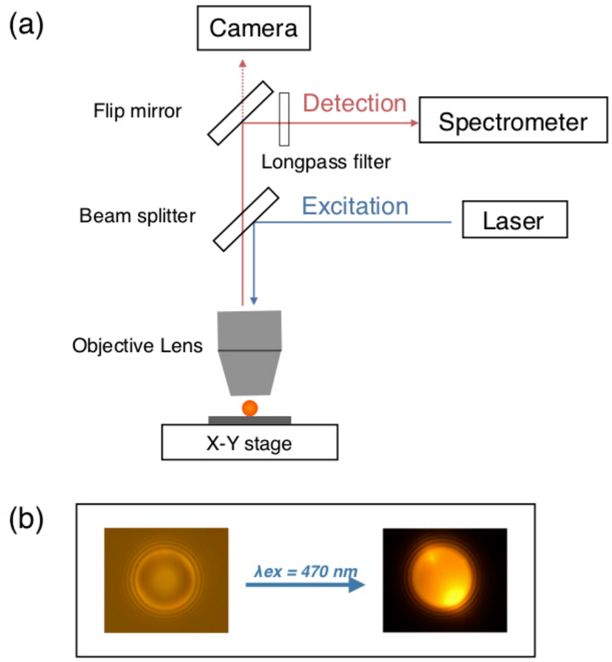


Fig. S24. (a) A schematic illustration of the experiment setup of μ-PL measurement. (b) Microscopic images of a **PAA-TPE** microsphere under illumination by backlight (left) and laser excitation (right, λ_{ex} = 470 nm)

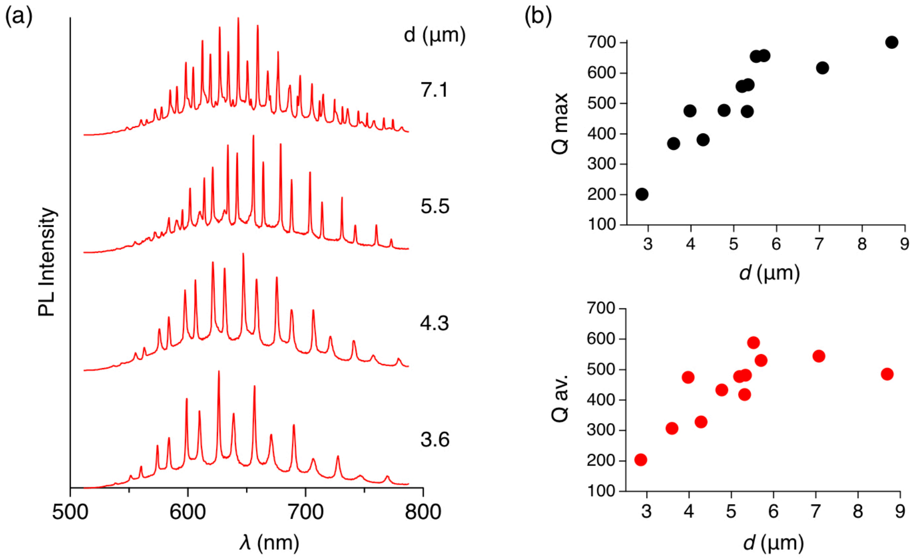


Fig. S25. (a) Size dependent μ-PL spectra of **PAA-TPE** microspheres. The values at the right side of the spectra indicate the diameter of the microspheres. (b) Plots of maximum and averaged Q values (Q_{max} and Q_{av}, respectively) against diameter (*d*) of the microspheres (λ_{ex} = 470 nm).

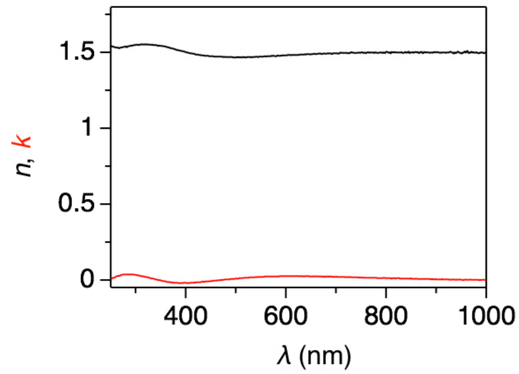


Fig. S26. Real (black) and imaginary (red) parts of the refractive indices of a thin film of **PAA-TPE** measured by spectroscopic ellipsometry.

7. Humidity-dependent μ-PL spectroscopy

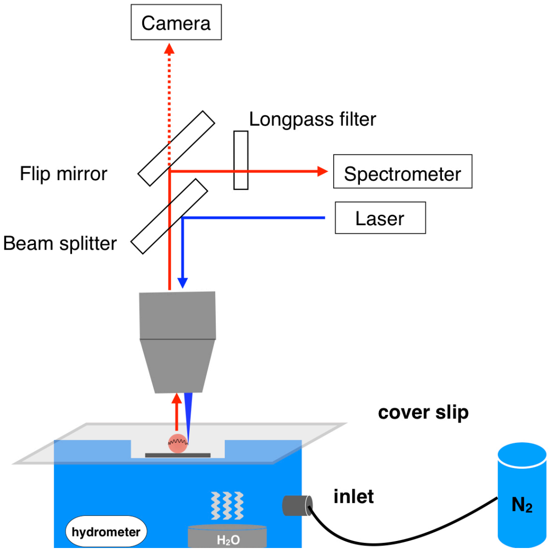


Fig. S27. A schematic drawing of the humidity testing setup equipped under a home-made μ-PL measurement system.

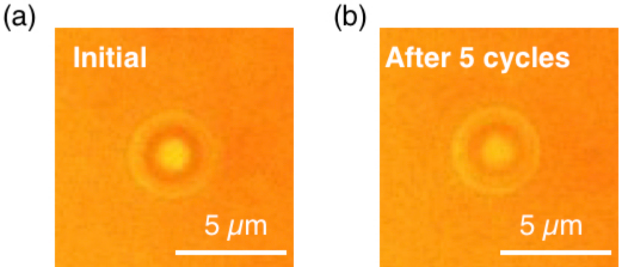


Fig. S28. Microscopic images of a **PAA-TPE** microsphere taken before and after 5 cycles of hydration and dehydration cycles.

8. Reference

[1] K. Li, W. Qin, D. Ding, N. Tomczak, J. Geng, R. Liu, J. Liu, X. Zhang, H. Liu, B. Liu, B. Z. Tang *Sci*. *Rep*. 2013, **3**, 1150.