Supporting Information

New Thermally Stable Piezofluorochromic Aggregation-Induced Emission Compounds

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Contents

1. Materials and Measurements

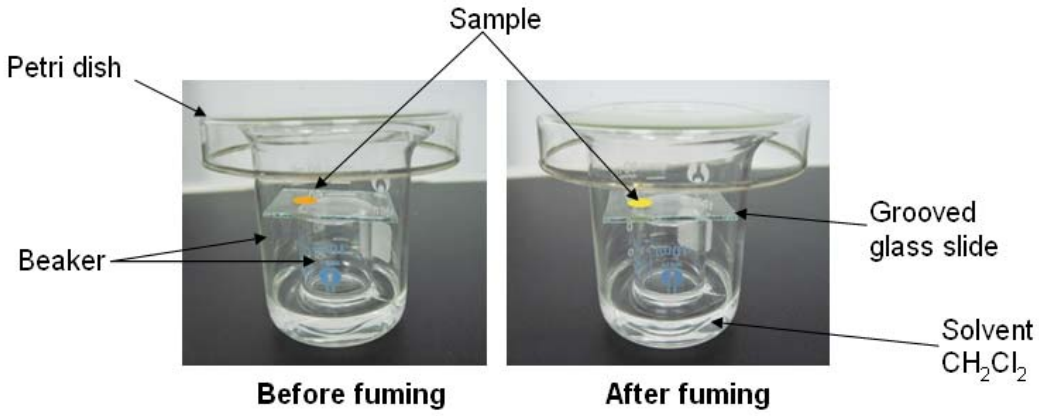
9,10-bis(chloromethyl)anthracene, 9,10-dibromoanthracene, *p*-tolylboronic acid, N-bromosuccinimide (NBS), benzoyl peroxide (BPO), triethyl phosphite, potassium *tert*-butoxide (*t*-BuOK), bis(4-fluorophenyl)methanone, 9*H*-carbazole, diethyl 4-bromobenzylphosphonate, 4-formylphenylboronic acid, 1-formylpiperidine, tetrabutyl ammonium bromide (TBAB), *n*-butyl-lithium in hexane (2.2M), tetrakis(triphenylphosphine) palladium(0) trimethyl borate, phosphorus chloride oxide ($POCl_3$), potassium iodide (KI), potassium iodate (KIO_3) and potassium carbonate (K_2CO_3) purchased from Alfa Aesar were used as received. Triphenylamine was obtained from Zhenjiang Haitong Chemical Industry Co., Ltd. (China). All other reagents and solvents were purchased as analytical grade from Guangzhou Dongzheng Company (China) and used without further purification.

Intermediate **1** was synthesized according to the literature method.[1] Intermediates **4**, and **5** were prepared according to the literature procedures.[2] Intermediates **6**, **7**, **8** and **10** were synthesized according to procedures in the literature previously published by us.[3]

Proton and carbon nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR) spectra were measured on a Mercury-Plus 300 spectrometer [$CDCl_3$, tetramethylsilane (TMS) as the internal standard]. High resolution mass spectrum (HRMS) was measured on a Thermo MAT95XP-HRMS spectrometer. The target compounds An-1a and An-2a have not obtained the HRMS spectra due to their high molecular weight (>3000 g/mol). Elemental analyses (EA) were performed with an Elementar Vario EL elemental analyzer. Photoluminescence spectra (PL) were measured on a Shimadzu RF-5301pc spectrometer with a slit width of 1.5 nm for both excitation and emission. Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204 F1) at a heating rate of 10 °C/min under N_2 atmosphere. Thermogravimetric analyses (TGA) were carried out using a thermal analyzer (Shimadzu, TGA-50H) under N_2 gas flow with a heating rate of 20 °C/min. Wide-angle X-ray diffraction (WAXD) measurements were performed by using a

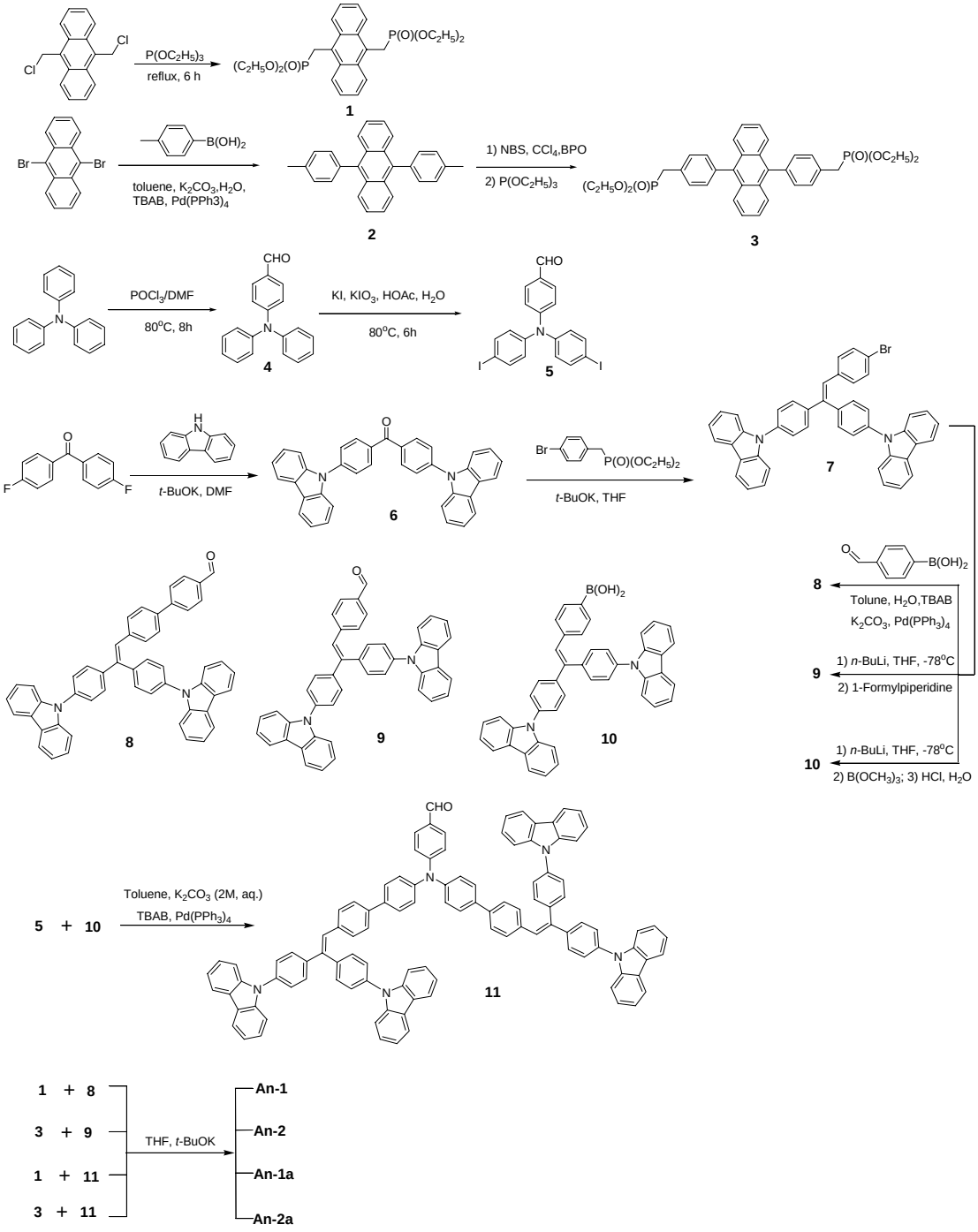
Rigaku X-ray diffractometer (D/max-2200) with an X-ray source of Cu Kα(λ= 0.15406 nm) at 40 kV and 30 mA, at a scan rate of 4° (2θ) per 1min. Time-resolved emission decay behaviors were measured on an Endinburgh Instruments Ltd spectrometer (FLSP920) and the data were processed according to the literature method.[4] Pressed samples were prepared by pressing in an an IR pellet press at 1500 psi for 5 min or by grinding using a mortar and pestle. Annealing experiments were done on a hot-stage with automatic temperature control system at 300 ^{o}C for 5 min. The water-THF mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature. For example, a 70% water fraction mixture was prepared in a volumetric flask by adding 7 mL distilled water into 3 mL THF solution of the sample. The concentrations of all samples were adjusted to 10 μM after adding distilled water. The fluorescence quantum yields of all the compounds in pure THF or THF/water mixtures were evaluated using quinine sulfate as the reference.[5]

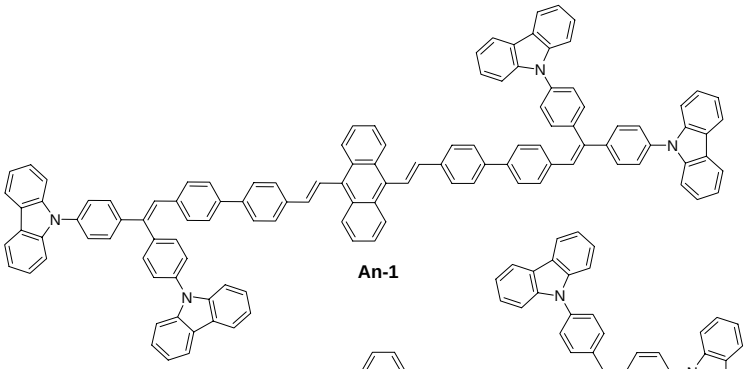
The experiment of solvent vapors fuming treatment is illustrated in Scheme S1. The sample was filled on a grooved glass slide, which was then placed in a large beaker saturated with CH_2Cl_2 vapors for 5 min at room temperature.



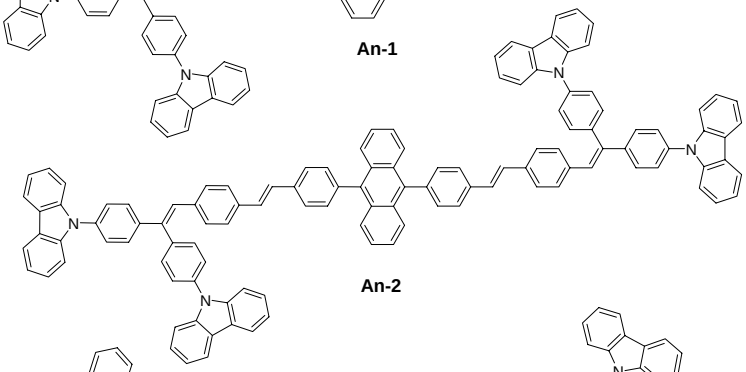
Scheme S1. Photographs of the fuming experiment.

2. Synthesis

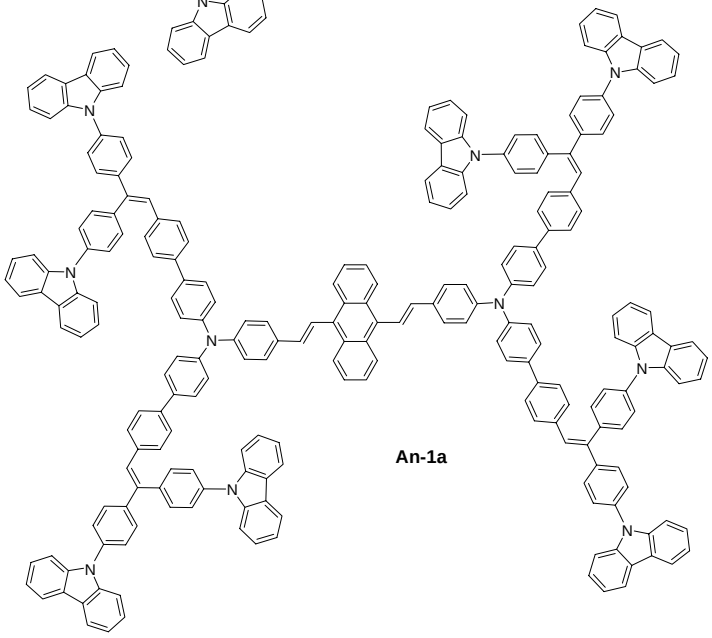

P(OC2H5)3
reflux, 6 h
(C2H5O)2(O)P
P(O)(OC2H5)2
1
B(OH)2
toluene, K2CO3,H2O,
TBAB, Pd(PPh3)4
2
1) NBS, CCl4,BPO
2) P(OC2H5)3
3
POCl3/DMF
80°C, 8h
4
KI, KIO3, HOAc, H2O
80°C, 6h
5
t-BuOK, DMF
6
t-BuOK, THF
7
8
Tolune, H2O,TBAB
K2CO3, Pd(PPh3)4
9
1) n-BuLi, THF, -78°C
2) 1-Formylpiperidine
10
1) n-BuLi, THF, -78°C
2) B(OCH3)3; 3) HCl, H2O
5 + 10
Toluene, K2CO3 (2M, aq.)
TBAB, Pd(PPh3)4
11
1 + 8
3 + 9
1 + 11
3 + 11
THF, t-BuOK
An-1
An-2
An-1a
An-2a



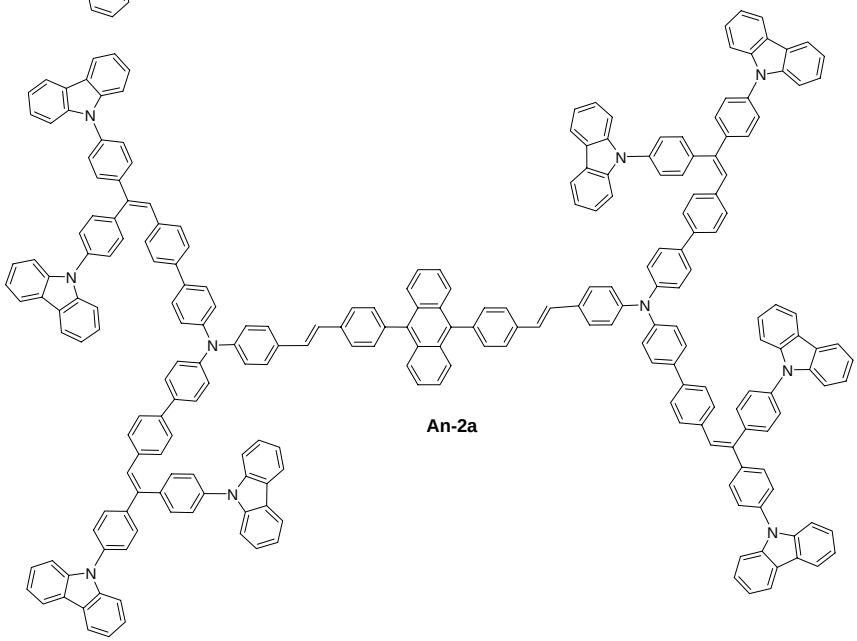
An-1



An-2



An-1a



An-2a

Scheme S2. Synthetic route of the compounds.

*2.1. Synthesis of **2***

9,10-Dibromoanthracene (2.8 g, 8.3 mmol) and p-tolylboronic acid (2.72 g, 20 mmol) were dissolved in the mixture of toluene (60 mL), TBAB (0.01 g) and 2M potassium carbonate aqueous solution (18 mL). The mixture was stirred at room temperature for 0.5 h under Ar gas followed adding $Pd(PPh_3)_4$ (0.010 g, 8.70×10^{-3} mmol) and then heated to 90°C for 24 h. After that the mixture was poured into water and extracted three times with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with *n*-hexane as eluent to give **2** (2.83 g, 95% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δppm: 2.56 (s, 6H), 7.28-7.45 (m, 12H), 7.67-7.79 (m, 4H).

*2.2. Synthesis of **3***

A mixture of **2** (2.01 g, 5.6 mmol), NBS (3.0 g, 16.8 mmol), and benzoyl peroxide (0.071 g, 0.29mmol) in CCl_4 (40mL) was refluxed for 4 h. The mixture was filtrated to remove the excessive NBS, after removing the solvent from the filtrate under reduced pressure, this intermediate was added to triethyl phosphite (15mL), and the resulting mixture was refluxed for 6 h. The solvent was removed in vacuum, and the residue was purified by a column chromatography on silica gel using ethyl acetate/CH_2Cl_2 (1:10) as eluent to give **3** (2.03 g, 57% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δppm: 1.24 (t, 12H, J=7.2 Hz), 3.39 (s, 2H), 3.46 (s, 2H), 3.99-4.12 (m, 8H), 7.35-7.47 (m, 8H), 7.51-7.61 (m, 8H).

*2.3. Synthesis of **9***

To a stirred solution of **7** (2.0 g, 3.0 mmol) in anhydrous THF (40 mL) was added n-butyllithium solution in hexane (2.2 M, 2.73mL, 6.0 mmol) dropwise slowly at -78 ^{o}C. The mixture was stirred at -78 ^{o}C under Ar gas for an additional 2 h. 1-Formylpiperidine (0.70mL) was added quickly at -78 ^{o}C and the mixture was stirred for 4 h allowing the temperature to rise gradually to room temperature. The product

was extracted into dichloromethane (3×20mL). The organic layer was separated and dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with *n*-hexane/ CH_2Cl_2 (1:1 by volume) as eluent to give **9** (1.48 g, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δppm: 7.22 (s, 1H), 7.27-7.37 (m, 6H), 7.40-7.57 (m, 10H), 7.60-7.80 (m, 8H), 8.17 (d, 4H, J=7.8 Hz), 9.97 (s, 1H); MS (EI) calcd. for $C_{45}H_{30}N_2O$ 614, found 614.

*2.4. Synthesis of **11***

5 (1.58 g, 3.0 mmol) and the boric acid **10** (6.0 mmol) in toluene (50 mL), 2M aqueous K_2CO_3 solution (9 mL) and 0.1 g of TBAB were added. The mixture was stirred for 40 min under an argon atmosphere at room temperature. Then the $Pd(PPh_3)_4$ catalyst (catalytic amount) was added and the reaction mixture was stirred at 90^{o}C for 16 h. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography with CH_2Cl_2: *n*-hexane = 2 : 3. Yellow power was obtained in the yield of 67%. ^{1}H-NMR (300 MHz, $CDCl_3$) δppm: 7.12-7.17 (d, 2H), 7.242(d, 4H), 7.26-7.35 (m, 12H), 7.41-7.75 (m, 44H), 8.17 (d, 8H), 9.84 (s, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δppm: 110.00, 110.10, 120.30, 120.60, 123.75, 126.15, 126.45, 126.65, 127.05, 127.60, 128.30, 129.20, 129.90, 130.45, 131.55, 132.20, 136.40, 137.20, 137.45, 139.00, 139.40, 141.00, 141.35, 142.00, 145.65, 153.10, 190.50; FT-IR (KBr) υ (cm^{-1}): 3034, 2361, 1690, 1596, 1506, 1493, 1447, 1331, 1318, 1221, 1163, 1007, 813, 748, 720, 671, 630, 561, 629. HRMS (FAB) m/z: 1443 ($[M]^+$, calcd for $C_{107}H_{71}N_5O$, 1443); Anal. Calc. for $C_{107}H_{71}N_5O$: C 89.08, H 4.96, N 4.85, O 1.11; Found: C 89.01, H 4.92, N 4.79.

2.5. Synthesis of ***An-1***

8 (0.17 g, 0.25 mmol) and **1** (0.053 g, 0.11 mmol) were dissolved in THF (10 mL), then *t*-BuOK (0.1 g) was added under Ar gas. The solution was stirred at room temperature overnight. After removing the solvent under reduced pressure, the residue was recrystallized with THF/EtOH to give **An-1** (0.16g, 93% yield). Melting point: 348 ^{o}C (Obtained from heating DSC curve, as-synthesized sample); ^{1}H NMR (300 MHz, $CDCl_3$) δppm: 6.97 (s, 1H), 7.02 (s, 1H), 7.26-7.37 (m, 14H), 7.41-7.80 (m, 48H), 7.97 (s, 1H), 8.03 (s, 1H), 8.18 (q, 8H, J=3.9 Hz), 8.42 (q, 4H, J=3.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δppm: 142.13, 141.82, 141.73, 141.32, 141.00, 140.22, 139.40, 137.65, 137.47, 132.23, 130.45, 129.81, 129.40, 129.22, 129.17, 127.63, 127.48, 127.30, 127.06, 126.86, 126.22, 125.58, 125.53, 123.76, 122.27, 121.11, 120.64, 120.33, 119.50, 118.73, 117.33, 116.32, 115.13, 114.68, 113.61, 112.89, 111.33, 110.09, 110.03; MS (FAB) calcd. for $C_{118}H_{78}N_4$ 1550, found 1551 $[M+H]^+$; Anal. calc. for $C_{118}H_{78}N_4$: C 91.32, H 5.07, N 3.61; Found: C 91.25, H 5.11, N 3.57.

2.6. Synthesis of ***An-2***

9 (0.245 g, 0.40 mmol) and **3** (0.10 g, 0.16 mmol) were dissolved in THF (15 mL), then *t*-BuOK (0.1 g) was added under Ar gas. The solution was stirred at room temperature overnight. After removing the solvent under reduced pressure, the residue was recrystallized with THF/EtOH to give **An-2** (0.20 g, 81% yield). Melting point: 369 ^{o}C (Obtained from heating DSC curve, as-synthesized sample); ^{1}H NMR (300 MHz, $CDCl_3$) δppm: 7.17-7.24 (m, 6H), 7.25-7.39 (m, 16H), 7.40-7.81 (m, 48H), 8.11-8.22 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δppm: 142.10, 141.62, 140.93, 139.43, 138.76, 138.29, 137.85, 137.43, 136.75, 135.28, 134.03, 132.22, 131.98, 130.85, 130.34, 129.36, 129.15, 128.73, 127.62, 127.16, 127.05, 126.78, 126.63, 126.22, 125.32, 123.76, 120.65, 120.34, 117.54, 117.52, 114.19, 113.18, 110.79, 110.09, 110.06; MS (FAB) calcd. for $C_{118}H_{78}N_4$ 1550, found 1551 $[M+H]^+$; Anal. calc. for $C_{118}H_{78}N_4$: C 91.32, H 5.07, N 3.61; Found: C 91.36, H 5.02, N 3.65.

2.7. Synthesis of ***An-1a***

1 (0.12 g, 0.25 mmol), and aldehyde **11** (0.72 g, 0.5 mmoL) were dissolved in anhydrous THF (10 mL). Then the mixtures were stirred under an argon atmosphere at room temperature. After 30 min, potassium tert-butyloxide (0.056 g, 0.5 mmoL) was added and the mixture was stirred for 4 h. The reaction mixture was concentrated and purified by silica gel column chromatography with CH_2Cl_2 : n-hexane (v:v, 1: 2). Orange power was obtained in yield of 81%. Melting point: 336 ^oC (Obtained from heating DSC curve, as-synthesized sample); ^{1}H-NMR (300 MHz, $CDCl_3$) δppm: 6.86-6.96 (d, 4H), 7.21-7.34 (m, 48H), 7.40-7.73 (m, 80H), 7.83-7.90 (d, 2H), 8.12-8.20 (d, 14H), 8.38-8.46 (dd, 4H); ^{13}C-NMR (75 MHz, $CDCl_3$) δppm: 110.05, 120.30, 120.65, 123.75, 124.70, 126.20, 126.48, 127.05, 127.65, 127.95, 128.20, 128.55, 128.80, 129.10, 129.85, 130.40, 130.75, 130.95, 131.20, 132.25, 132.95, 133.25, 133.42, 135.20, 135.95, 136.30, 137.05, 137.40, 139.40, 139.70, 139.90, 140.25, 140.95, 141.65, 142.10, 146.95, 153.90, 157.70; FT-IR (KBr) υ (cm^{-1}): 3034, 2924, 2853, 2354, 1590, 1506, 1447, 1318, 1227, 1169, 1104, 819, 742, 522; Anal. Calc. for $C_{230}H_{152}N_{10}$: C 90.40, H 5.01, N 4.58; Found: C 90.36, H 5.04, N 4.55.

*2.8. Synthesis of **An-2a***

11 (0.3 g, 0.22 mmol) and **3** (0.06 g, 0.10 mmol) were dissolved in THF (15 mL), then *t*-BuOK (0.22 mmol) was added under Ar gas. The solution was stirred at room temperature overnight. After removing the solvent under reduced pressure, the residue was recrystallized with THF/EtOH to give **An-2a** (0.29 g, 87% yield). No melting point of as-synthesized sample; ^{1}H-NMR (300 MHz, $CDCl_3$) δppm: 7.19 (s, 4H), 7.22-7.26 (m, 20H), 7.29-7.35 (m, 16H), 7.42-7.81 (m, 104H), 8.14-8.24 (dd, 16H).^{13}C-NMR (75 MHz, $CDCl_3$) δppm: 110.00, 110.10, 120.30, 120.50, 120.60, 121.55, 122.75, 122.85, 123.70, 124.50, 124.70, 125.30, 126.20, 126.50, 127.05, 127.60, 127.85, 129.15, 129.25, 129.90, 130.10, 130.40, 130.85, 131.10, 131.40, 131.55, 131.75, 131.95, 132.25, 132.40, 133.15, 133.30, 133.45, 133.80, 134.20, 134.60, 135.15, 135.95, 136.15, 136.25, 136.95, 137.10, 137.15, 137.35, 138.35, 138.50, 138.95, 139.30, 139.45, 140.50, 140.90, 141.10, 141.55, 142.10, 142.25, 142.40, 142.50, 143.20, 143.50, 143.95, 144.60, 146.95, 148.00. FT-IR (KBr) υ (cm^{-1}): 3025, 1595, 1510, 1491, 1448, 1359, 1333, 1311, 1227, 1168, 1018, 827, 743,

721, 626, 526. Anal. Calc. for $C_{242}H_{160}N_{10}$: C 90.61, H 5.03, N 4.37; Found: C 90.42, H 5.10, N 4.31.

3. References

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4. Table S1 and S2

Table S1. Thermal and photophysical properties of the compounds

compound	Tg[a] (°C)	Tm[a] (°C)	Td[b] (°C)	λem[c] (nm)	λem[d] (nm)
An-1	196	348	491	568	536
An-2	201	369	499	461	483
An-1a	223	336	516	554	560
An-2a	242	N/A	540	497	499

[a] obtained from DSC; [b] decompositon temperature at 5% weight loss; [c] determined in 10 μM dichloromethane solution; [d] determined in solid powder.

Table S2. Fluorescence decay parameters of the compounds before and after pressed

		τ_1 (ns) [a]	A_1 [b]	τ_2 (ns) [a]	A_2 [b]	$\langle\tau\rangle$ (ns) [c]
An-1	As-synthesized sample	0.80	0.88	2.13	0.12	0.96
	Pressed sample	1.05	0.75	2.17	0.25	1.33
An-2	As-synthesized sample	0.69	0.91	2.51	0.09	0.85
	Pressed sample	0.72	0.92	2.65	0.08	0.87
An-1a	As-synthesized sample	0.92	0.86	2.31	0.14	1.11
	Pressed sample	0.72	0.87	2.51	0.13	0.95
An-2a	As-synthesized sample	0.71	0.89	3.17	0.11	0.98
	Pressed sample	0.76	0.90	3.20	0.10	1.00

[a] Fluorescence lifetime; [b] fractional contribution; [c] weighted mean lifetime.

5. PL spectra of the dilute solutions of the compounds in water/THF mixtures with different water fractions

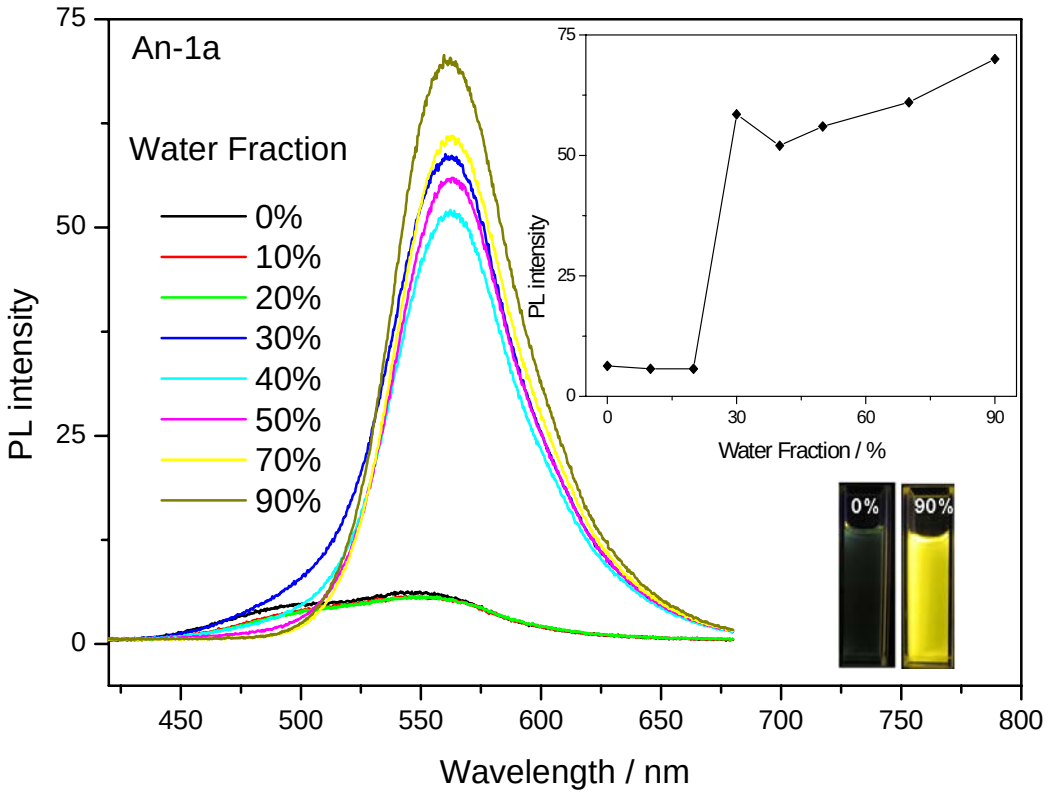


Figure S1. PL spectra of the dilute solutions of An-1a in water/THF mixtures with different water fractions (concentration: 10 μM; excitation wavelength: 365 nm). The inset depicts changes in PL peak intensity (up) and emission images of the compound in pure THF, and 90% water fraction mixtures under 365 nm UV illumination (down).

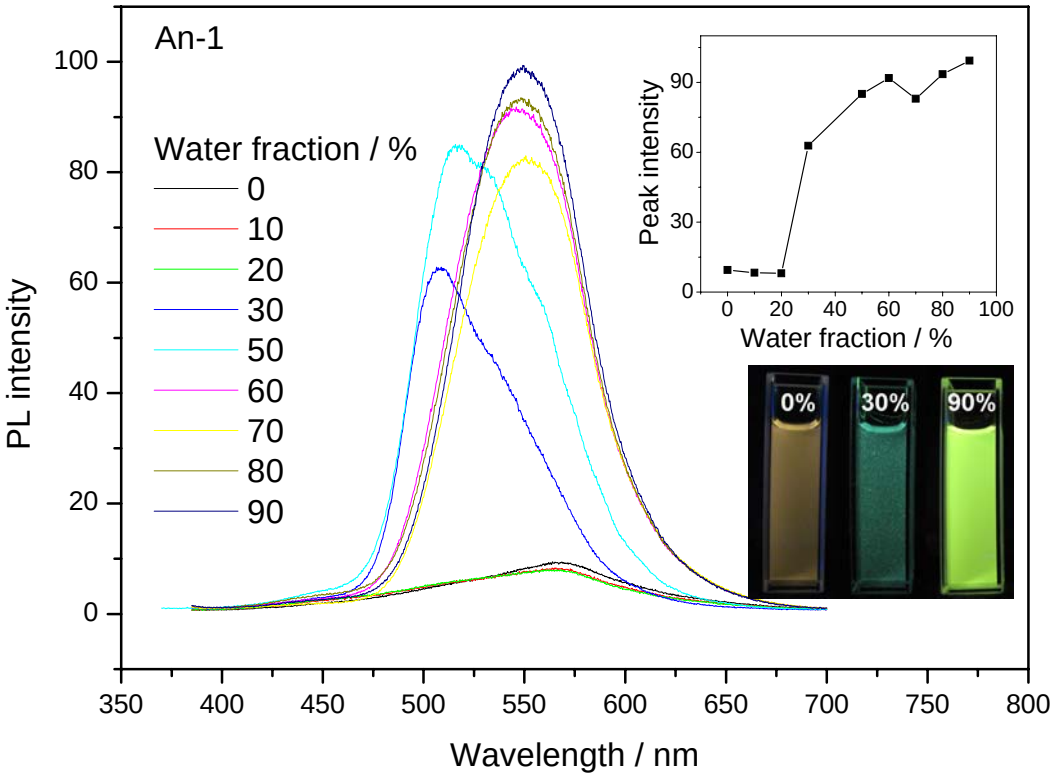


Figure S2. PL spectra of the dilute solutions of An-1 in water/THF mixtures with different water fractions (concentration: 10 μM; excitation wavelength: 365 nm). The inset depicts changes in PL peak intensity (up) and emission images of the compound in pure THF, 30% and 90% water fraction mixtures under 365 nm UV illumination (down).

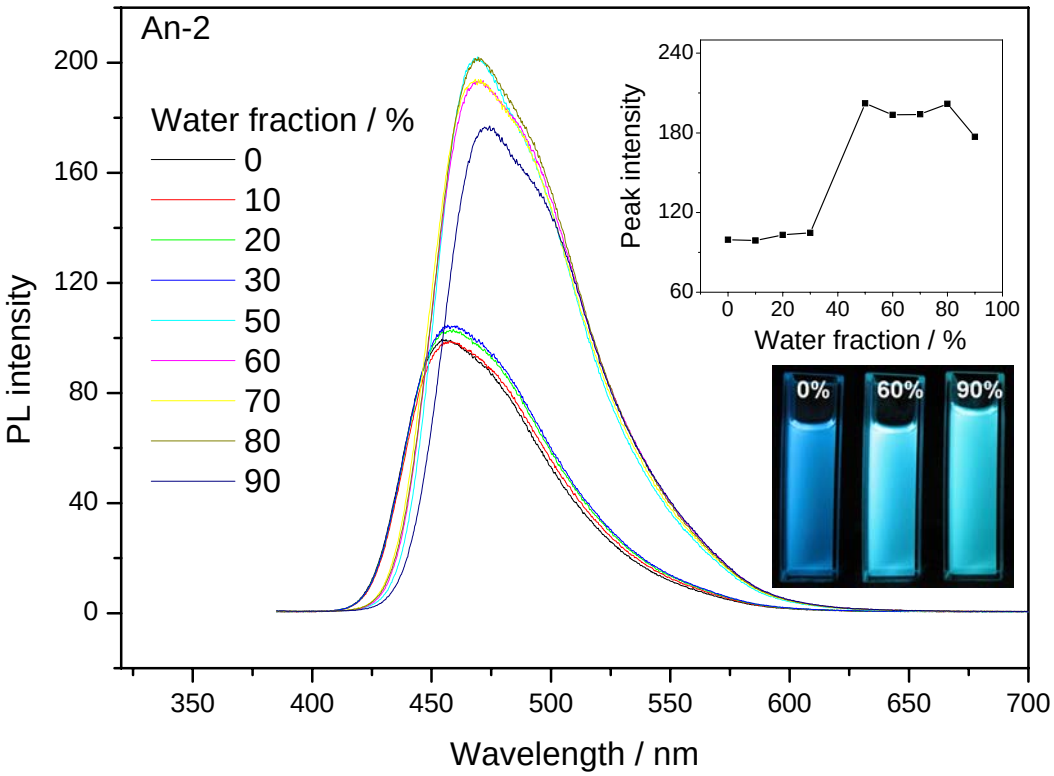


Figure S3. PL spectra of the dilute solutions of An-2 in water/THF mixtures with different water fractions (concentration: 10 μM; excitation wavelength: 365 nm). The inset depicts changes in PL peak intensity (up) and emission images of the compound in pure THF, 60% and 90% water fraction mixtures under 365 nm UV illumination (down).

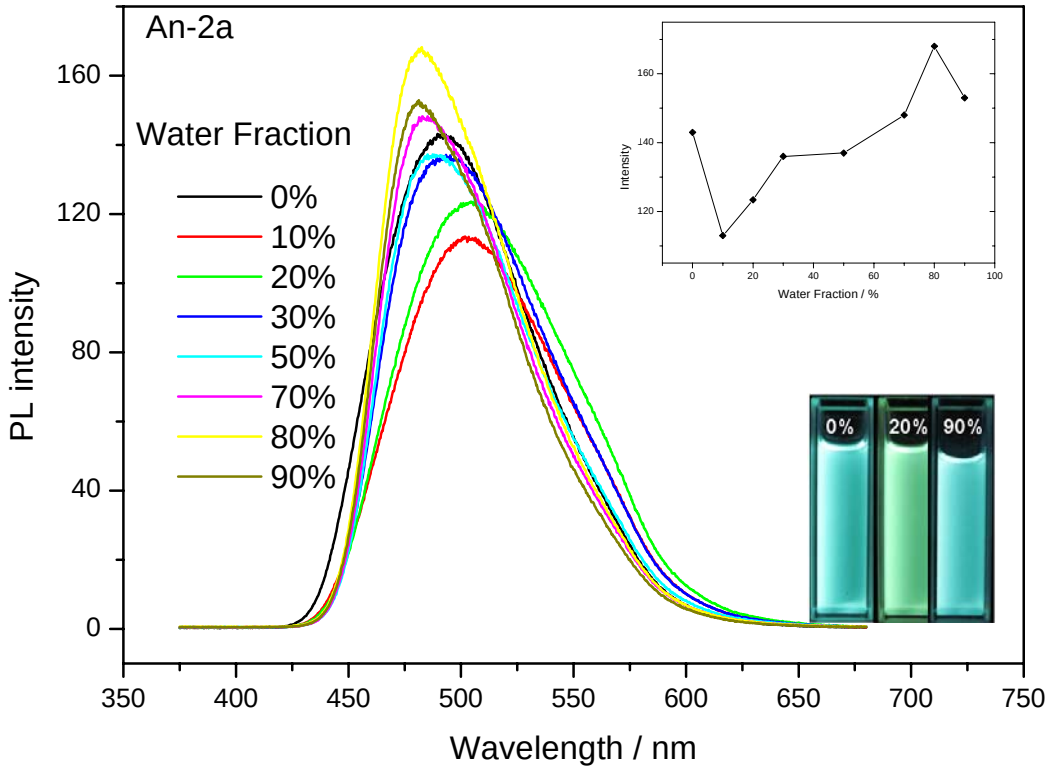


Figure S4. PL spectra of the dilute solutions of An-2a in water/THF mixtures with different water fractions (concentration: 10 μM; excitation wavelength: 365 nm). The inset depicts changes in PL peak intensity (up) and emission images of the compound in pure THF, 20% and 90% water fraction mixtures under 365 nm UV illumination (down).

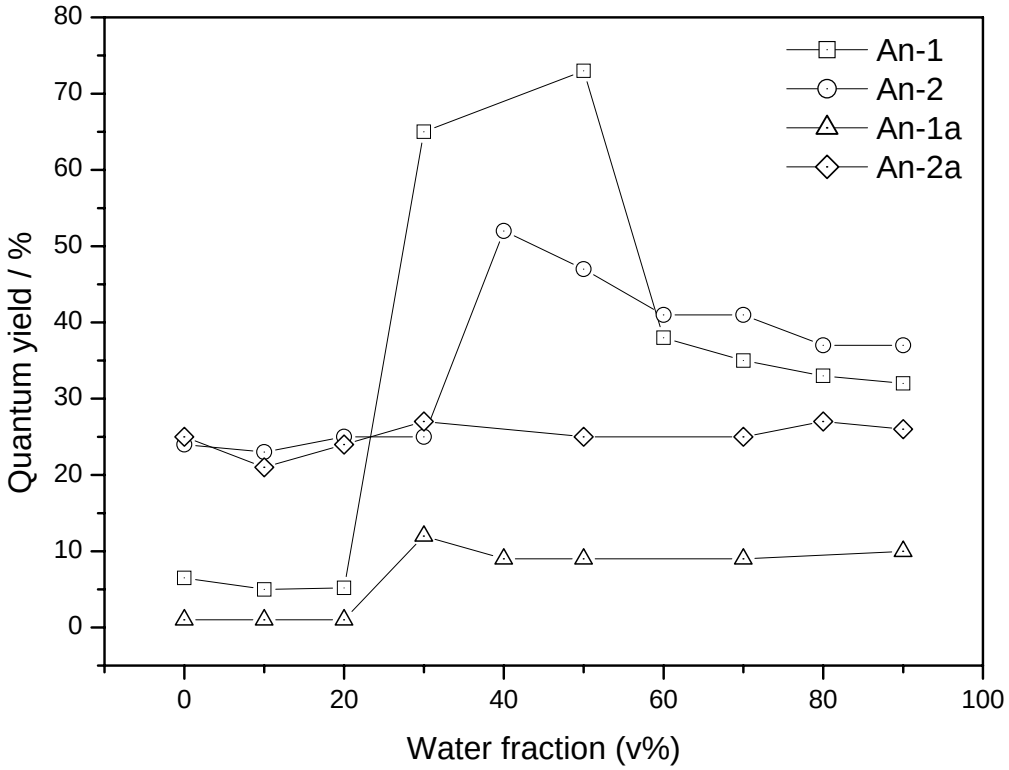


Figure S5. PL quantum yields of the compounds in water/THF mixtures with different water fractions (10 μM).

6. PL spectra and images of the samples obtained from annealing, pressing and fuming.

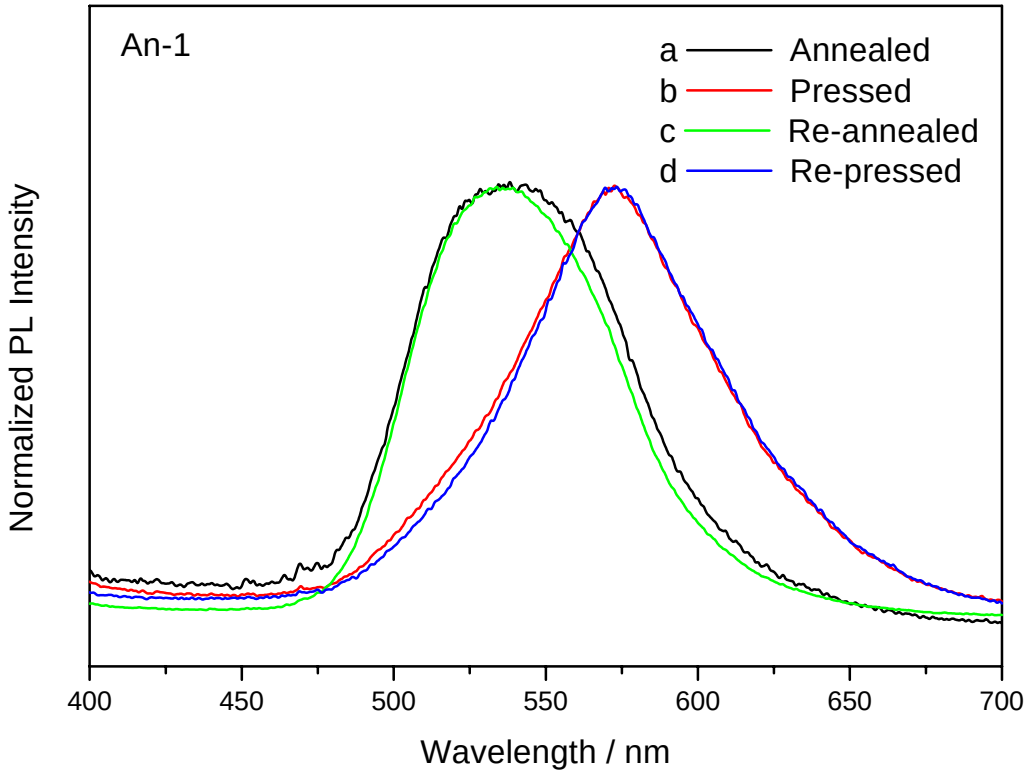


Figure S6. The normalized PL spectra of An-1 at room temperature after being (a) annealed; (b) pressed; (c) re-annealed; (d) re-pressed.

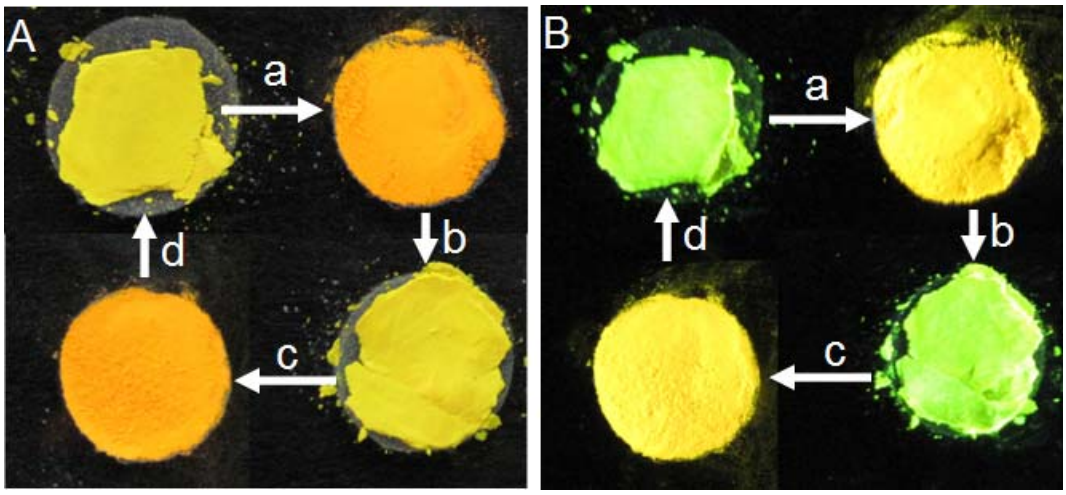


Figure S7. An-1 taken at room temperature under (A) natural light and(B) UV light after being (a) pressed; (b) annealed; (c) re-pressed; and (d) re-annealed.

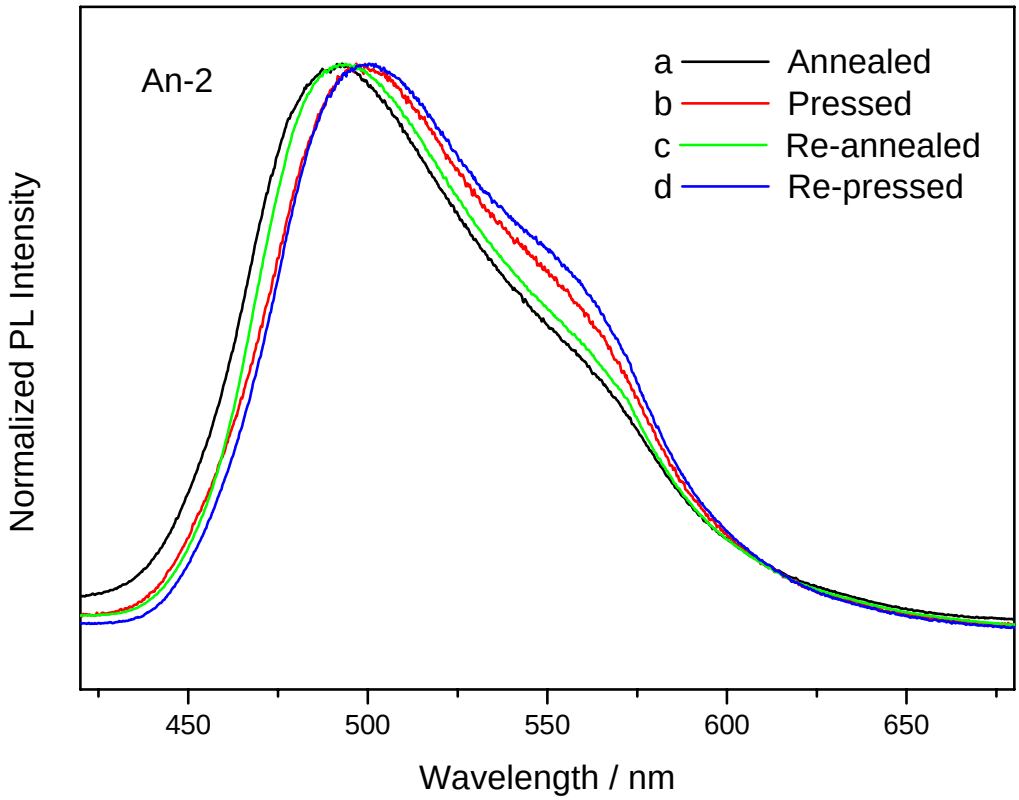


Figure S8. The normalized PL spectra of An-2 at room temperature after being (a) annealed; (b) pressed; (c) re-annealed; (d) re-pressed.

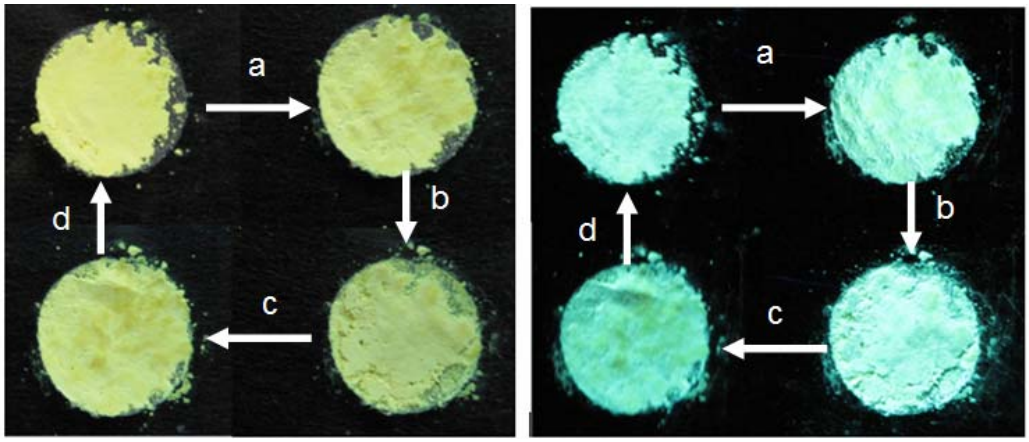


Figure S9. An-2 taken at room temperature under (A) natural light and(B) UV light after being (a) pressed; (b) annealed; (c) re-pressed; and (d) re-annealed.

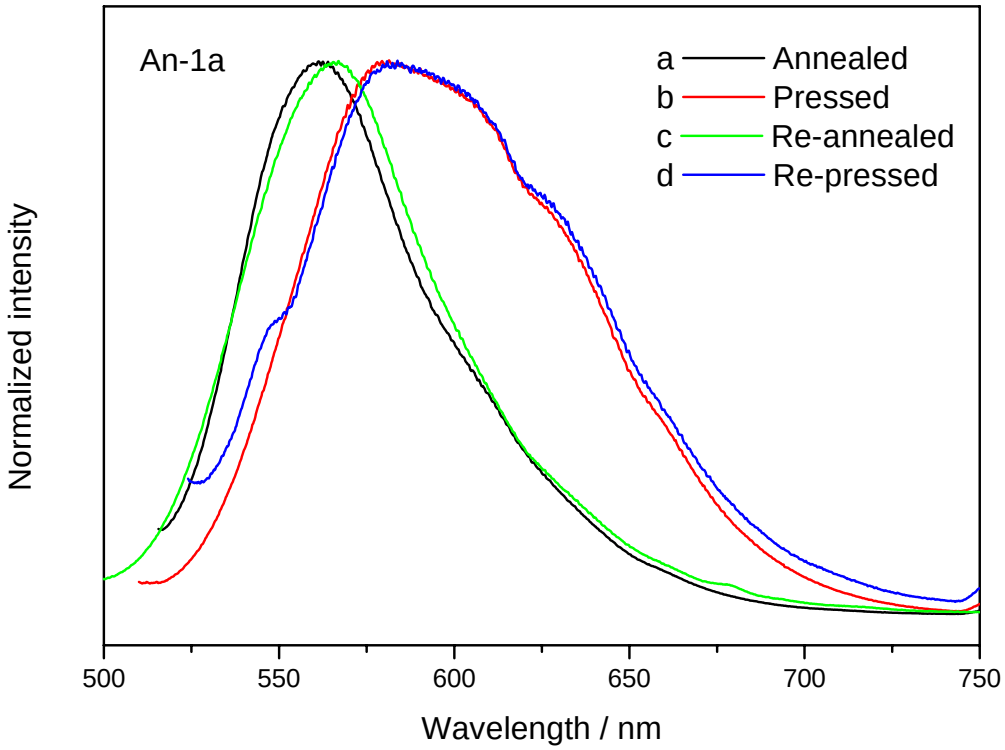


Figure S10. The normalized PL spectra of An-1a at room temperature after being (a) annealed; (b) pressed; (c) re-annealed; and (d) re-pressed.

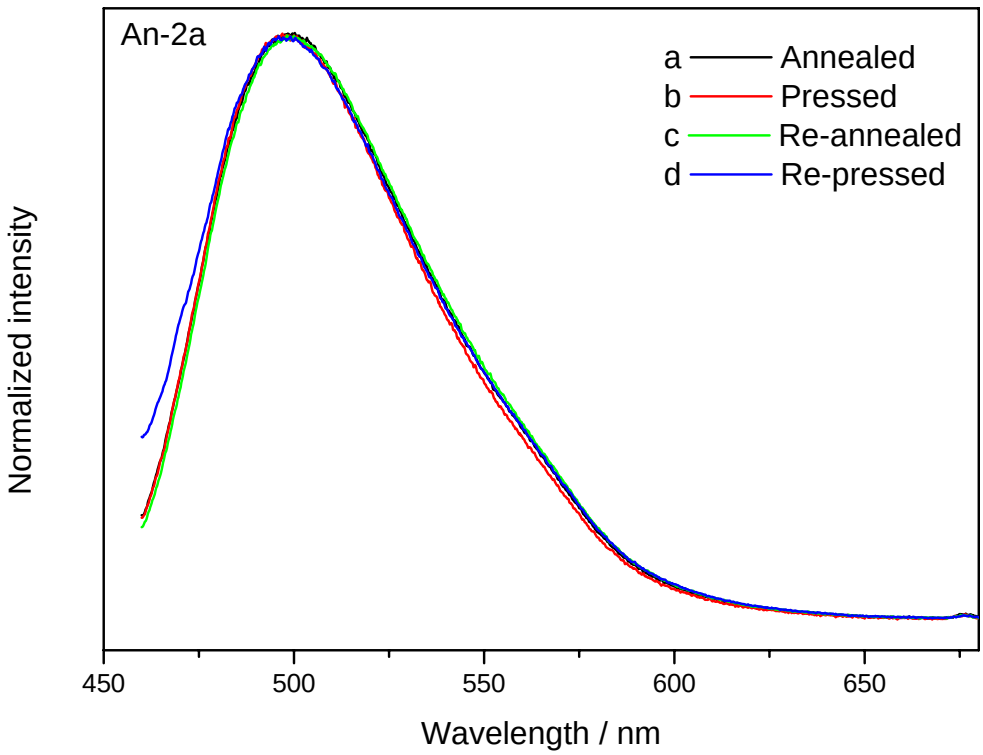


Figure S11. The normalized PL spectra of An-2a at room temperature after being (a) annealed; (b) pressed; (c) re-annealed; and (d) re-pressed.

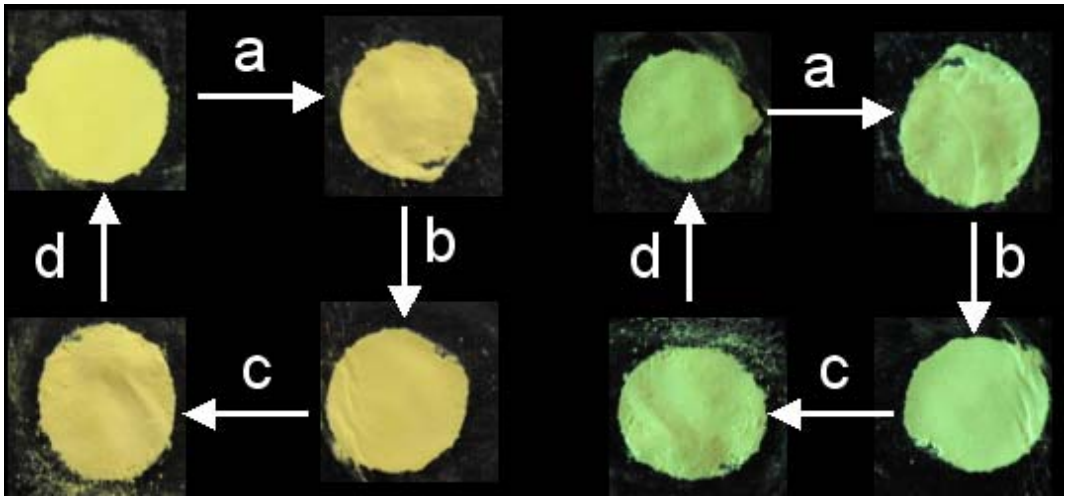


Figure S12. An-2a taken at room temperature under (A) natural light and(B) UV light after being (a) pressed; (b) annealed; (c) re-pressed; and (d) re-annealed.

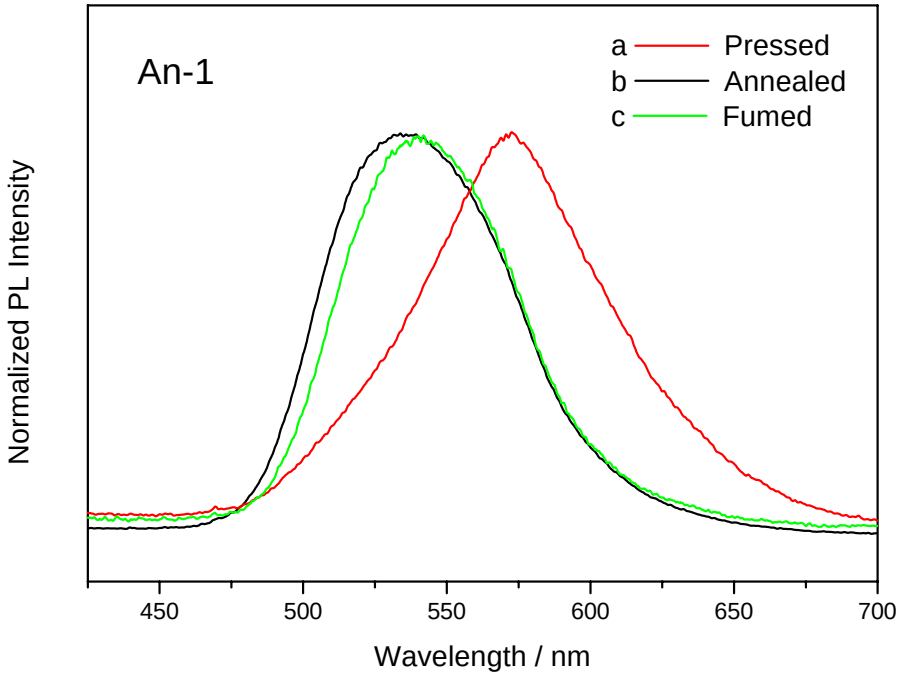


Figure S13. The normalized PL spectra of An-1 at room temperature: (a) pressed sample; (b) annealed the (a) sample; and (c) fumed the (a) sample with CH_2Cl_2.

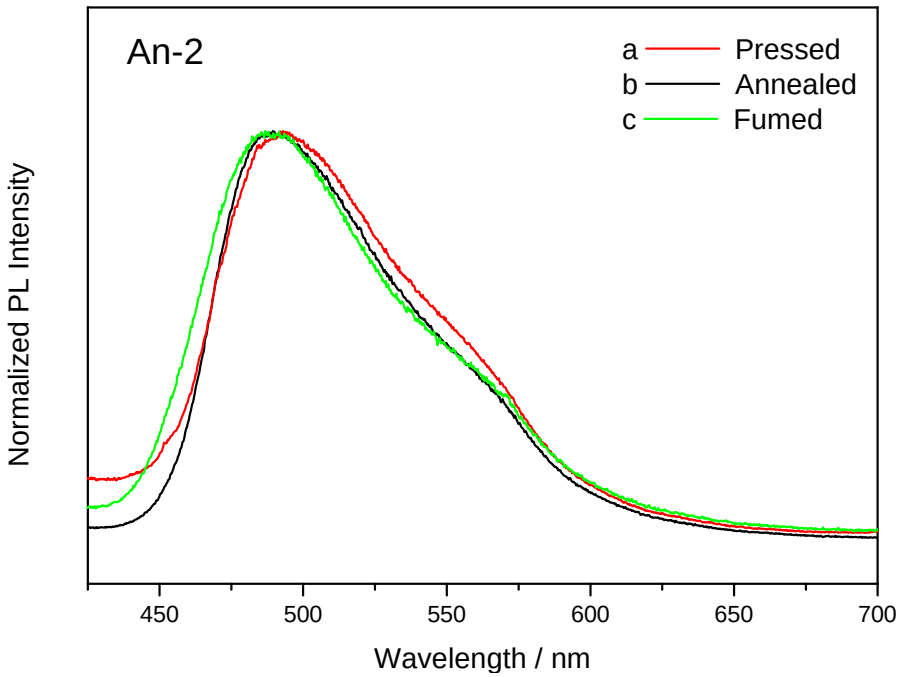


Figure S14. The normalized PL spectra of An-2 at room temperature: (a) pressed sample; (b) annealed the (a) sample; and (c) fumed the (a) sample with CH_2Cl_2.

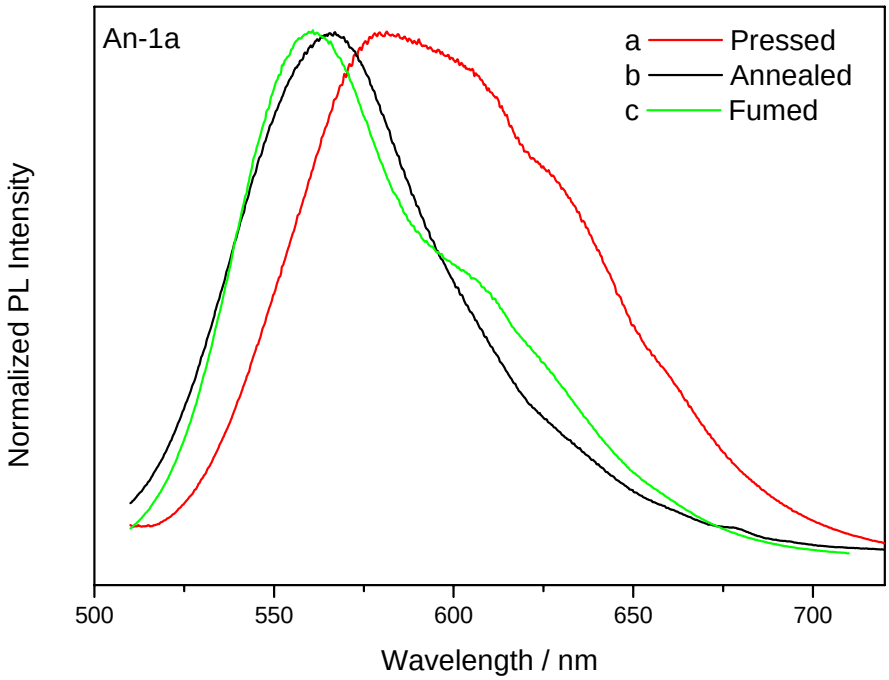


Figure S15. The normalized PL spectra of An-1a at room temperature: (a) pressed sample; (b) annealed the (a) sample; and (c) fumed the (a) sample with CH_2Cl_2.

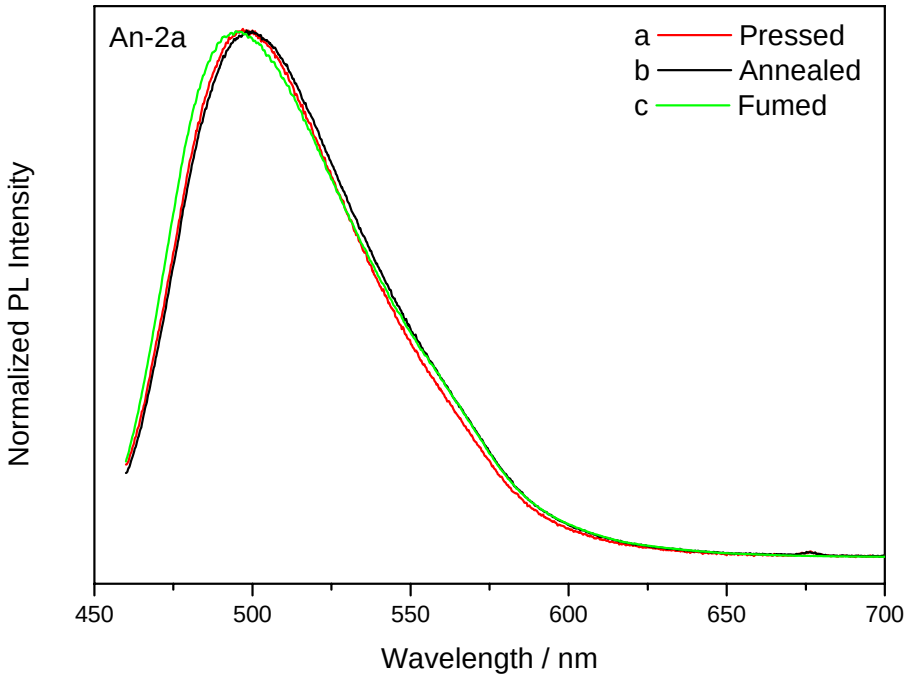
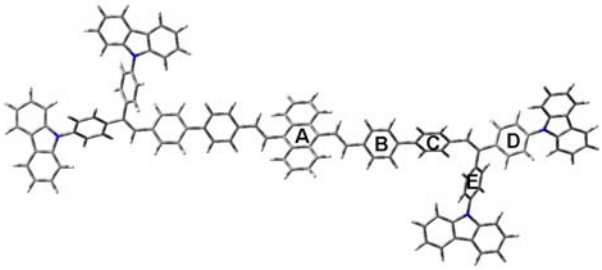
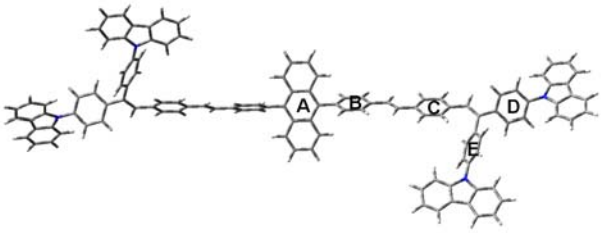


Figure S16. The normalized PL spectra of An-2a at room temperature: (a) pressed sample; (b) annealed the (a) sample; and (c) fumed the (a) sample with CH_2Cl_2.

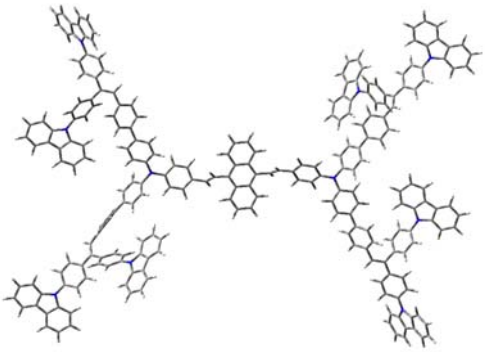
7. Lowest-energy conformers of the compounds



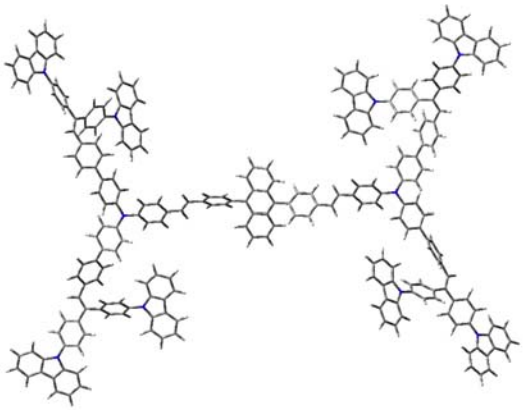
An-1
Dihedral angles: A-B 60º; C-D 68º; C-E 61º; D-E 75º



An-2:
Dihedral angles: A-B 76º; C-D:60º; C-E 62º; D-E:75º



An-1a



An-2a

Figure S17. Lowest-energy conformers of the compounds (optimized by MM2)

8. The WAXD curves of the compounds before and after pressing

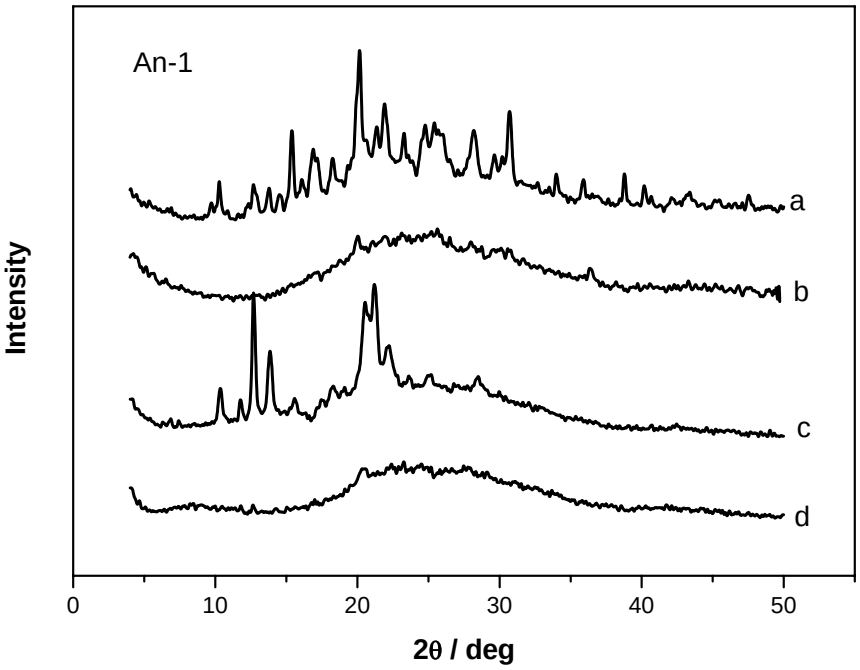


Figure S18. The WAXD curves of An-1 samples: (a) as-synthesized sample; (b) pressed sample; (c) annealing the pressed sample; (d) re-pressing the annealed sample.

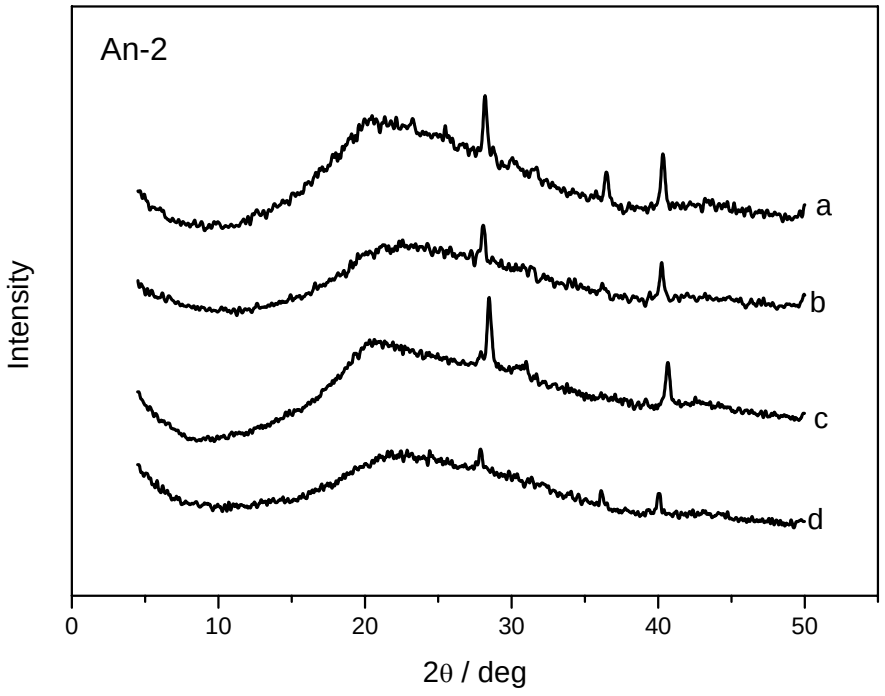


Figure S19. The WAXD curves of An-2 samples: (a) as-synthesized sample; (b) pressed sample; (c) annealing the pressed sample; (d) re-pressing the annealed sample.

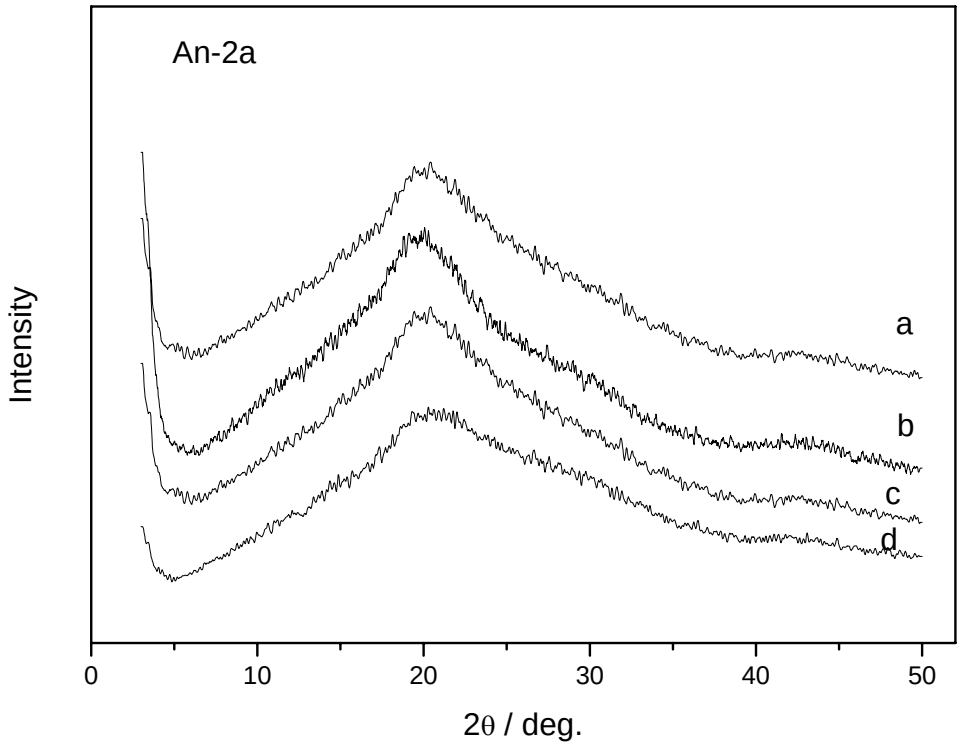


Figure S20. The WAXD curves of An-2a samples: (a) as-synthesized sample; (b) pressed sample; (c) annealing the pressed sample; (d) re-pressing the annealed sample.

9. The heating curves of the compounds before and after pressing

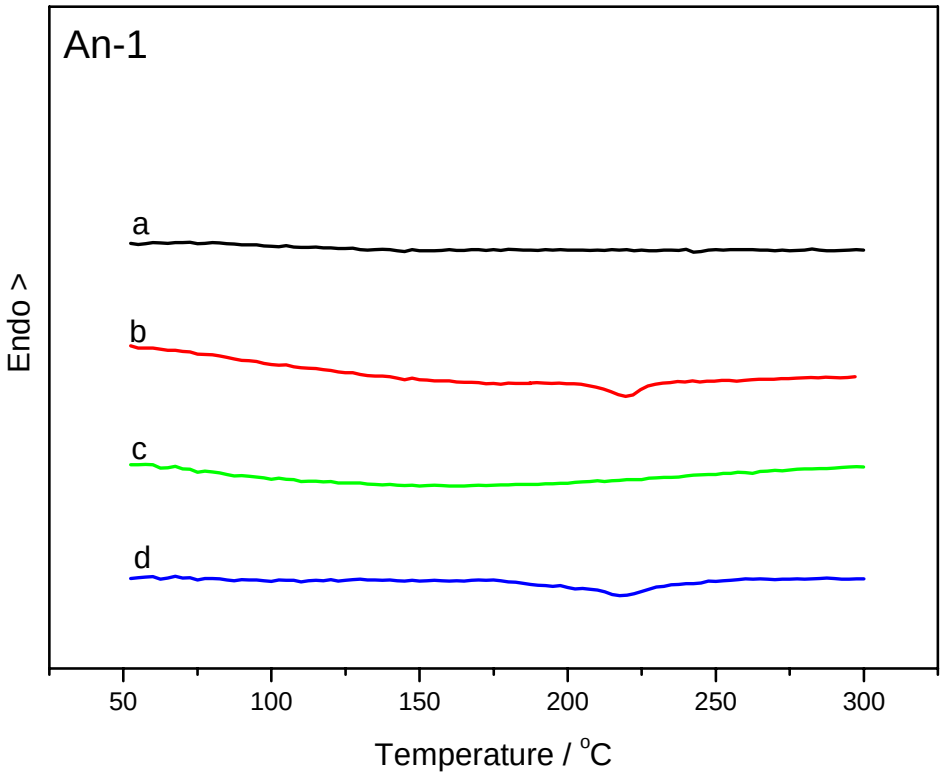


Figure S21. The heating DSC curves of An-1 samples: (a) as-synthesized sample; (b) pressed sample; (c) annealing the pressed sample; (d) re-pressing the annealed sample.

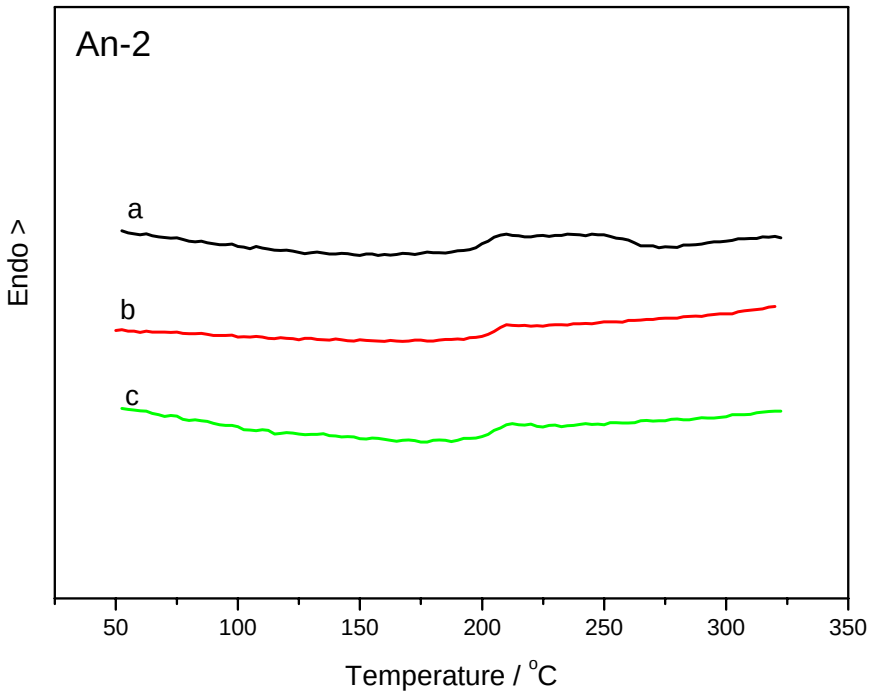


Figure S22. The heating DSC of An-2 samples: (a) as-synthesized sample; (b) annealed sample; (c) pressing the annealed sample.

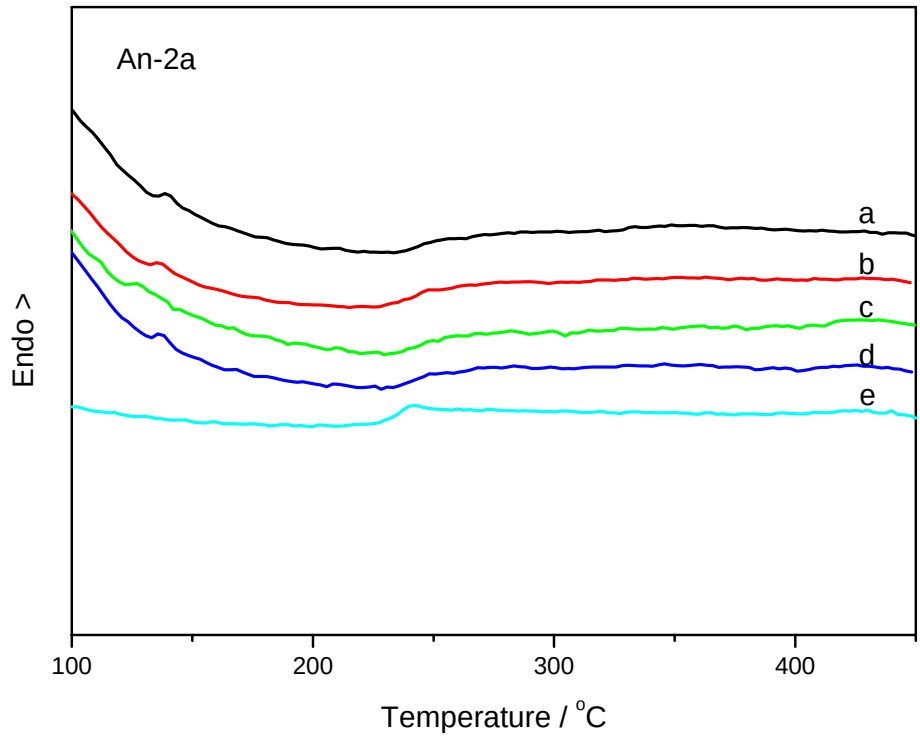


Figure S23. The heating DSC curves of An-2a: (a) as-synthesized sample; (b) pressed sample; (c) annealing the pressed sample; (d) re-pressing the annealed sample; (e) second heating after cooling the melt to room temperature at 10 °C/min.

10. PL spectra of the solid samples before and after pressing under different excitation wavelengths

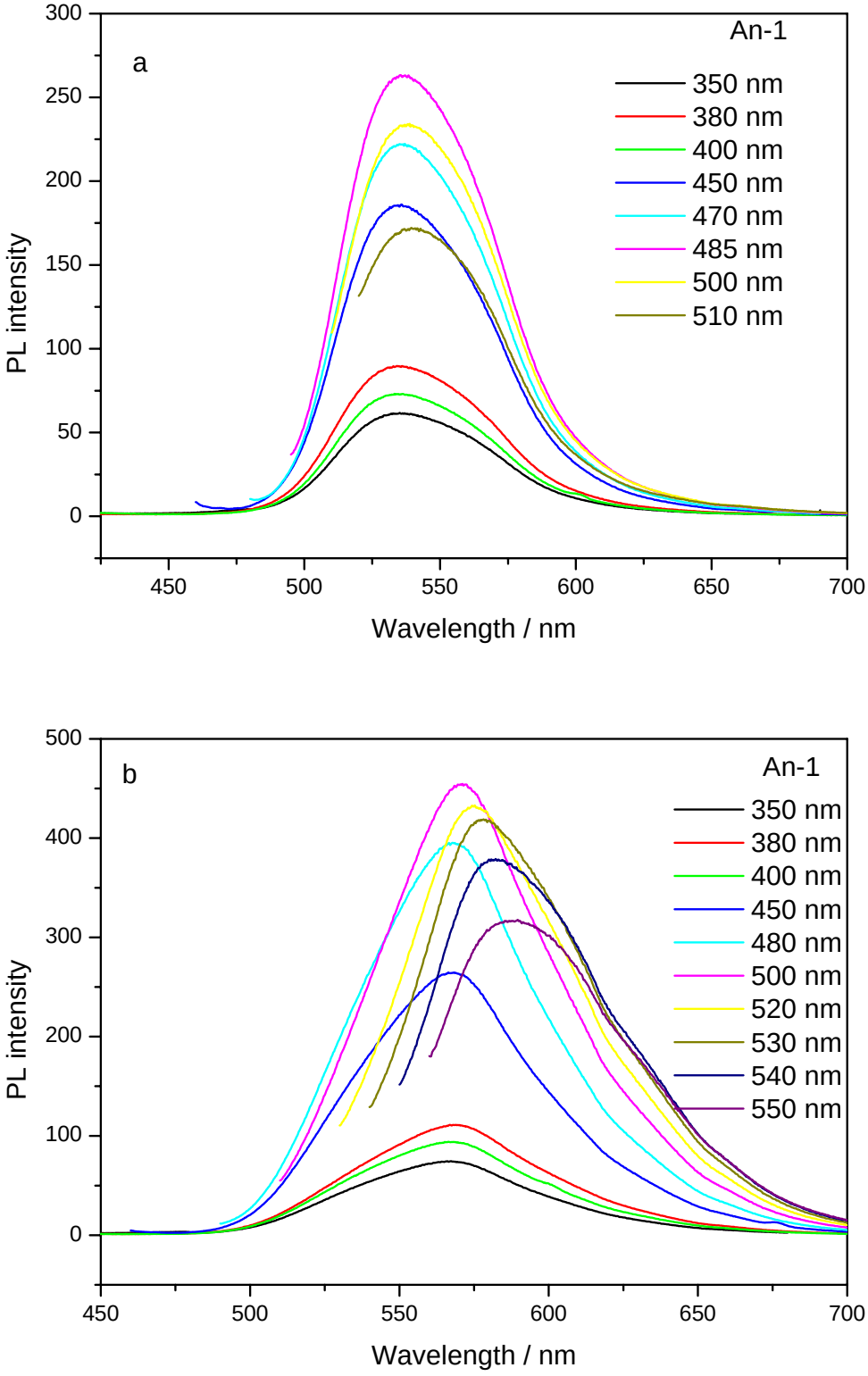


Figure S24. PL spectra of An-1 solid samples under different excitation wavelengths: (a) as-synthesized sample; (b) pressed sample.

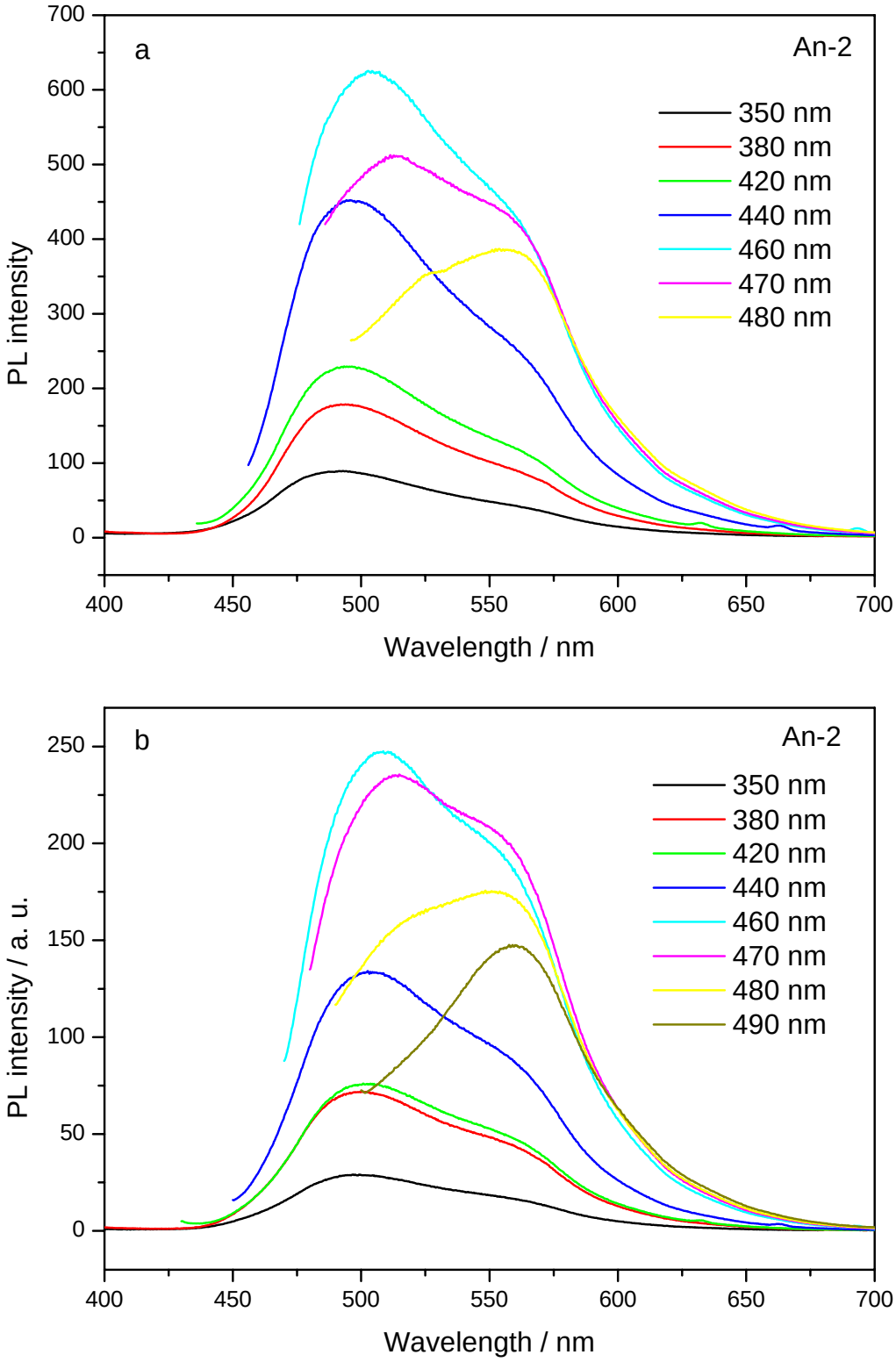


Figure S25. PL spectra of An-2 solid samples under different excitation wavelengths: (a) as-synthesized sample; (b) pressed sample.

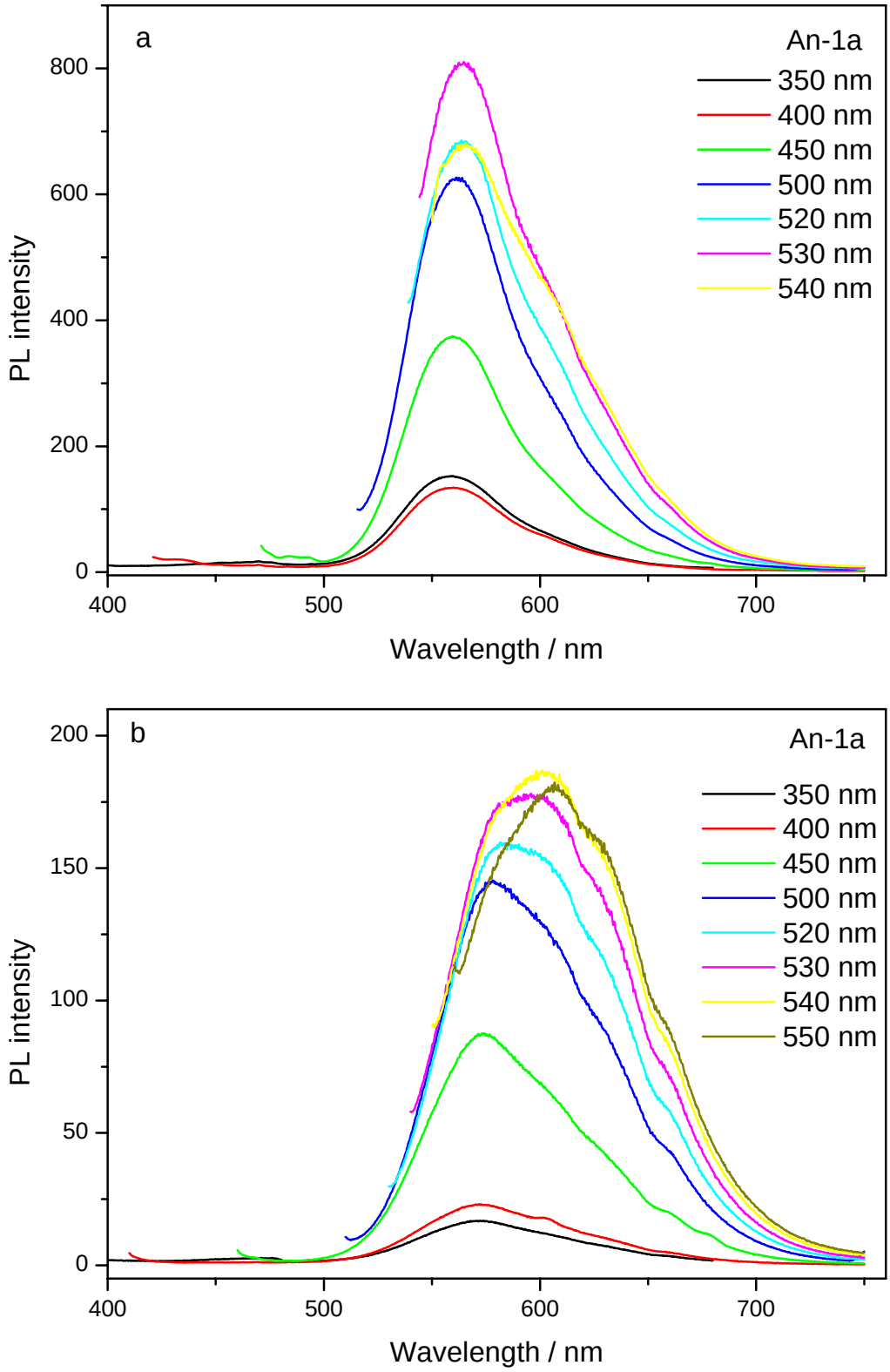


Figure S26. PL spectra of An-1a solid samples under different excitation wavelengths: (a) as-synthesized sample; (b) pressed sample.

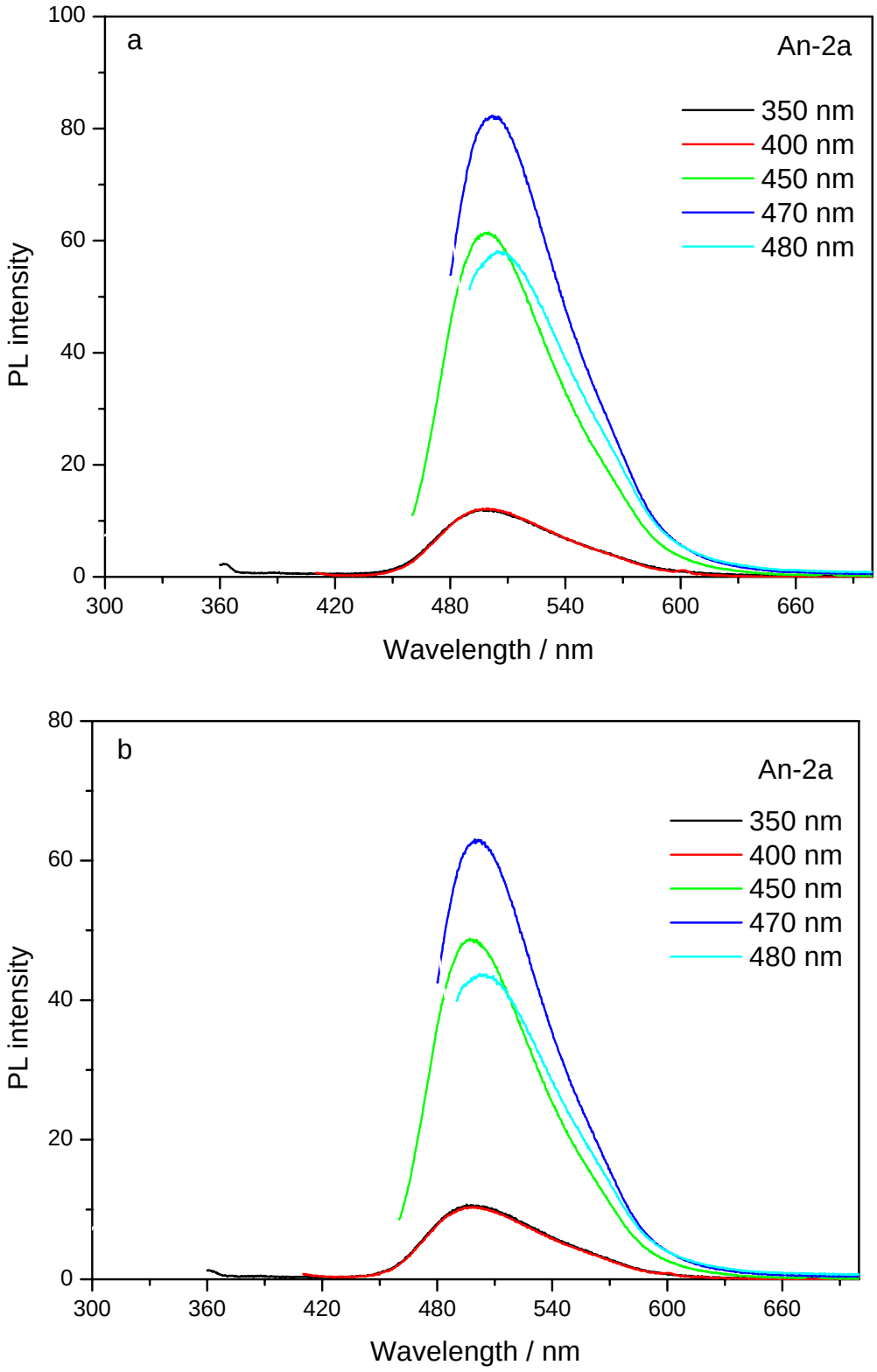


Figure S27. PL spectra of An-2a solid samples under different excitation wavelengths: (a) as-synthesized sample; (b) pressed sample.

11. Time-resolved emission decay spectra

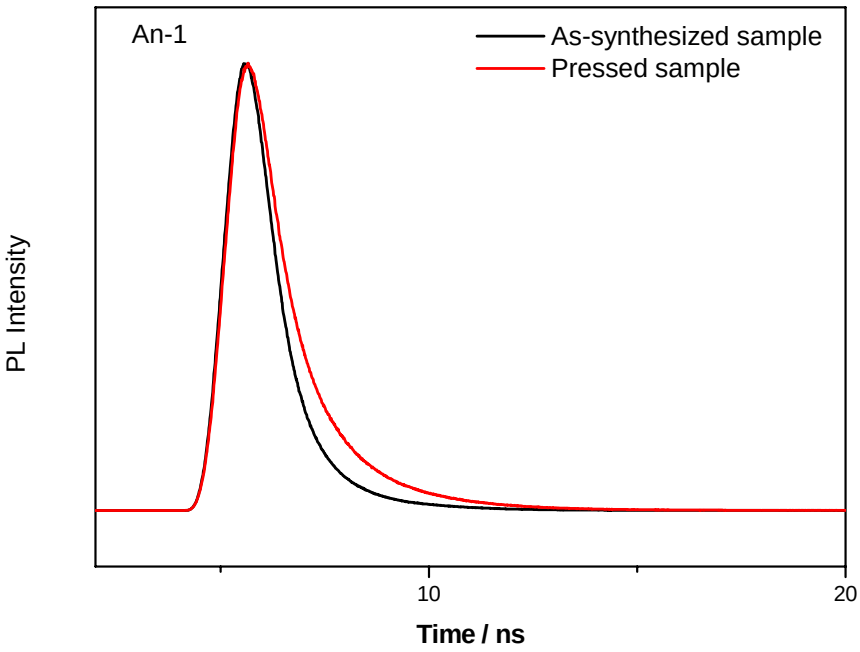


Figure S28. Time-resolved emission decay curves of An-1.

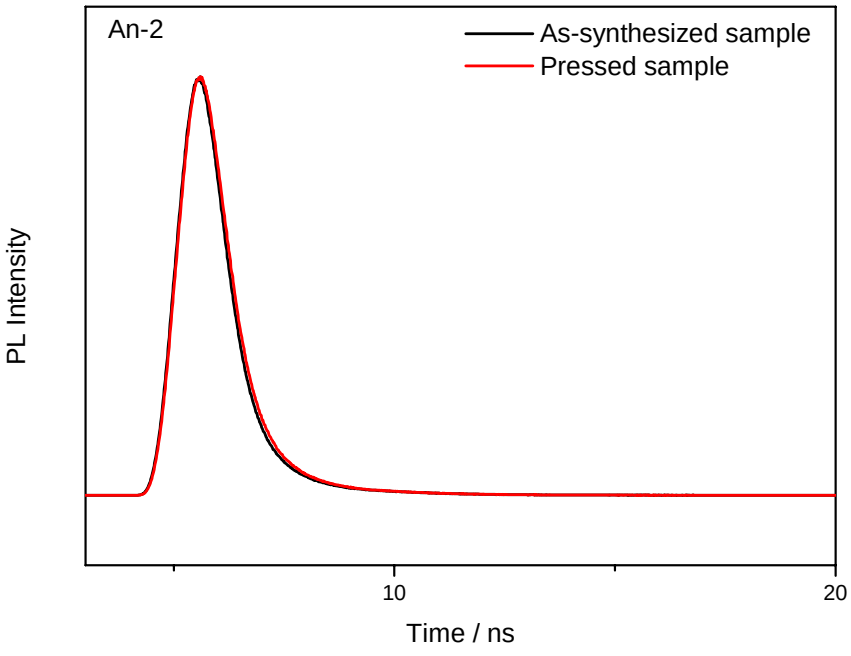


Figure S29. Time-resolved emission decay curves of An-2.

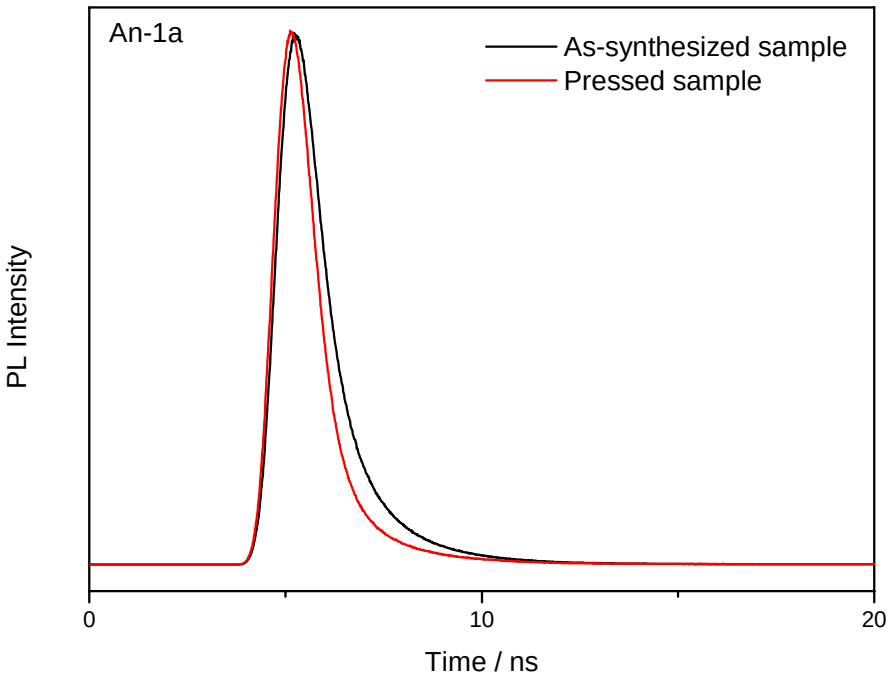


Figure S30. Time-resolved emission decay curves of An-1a.

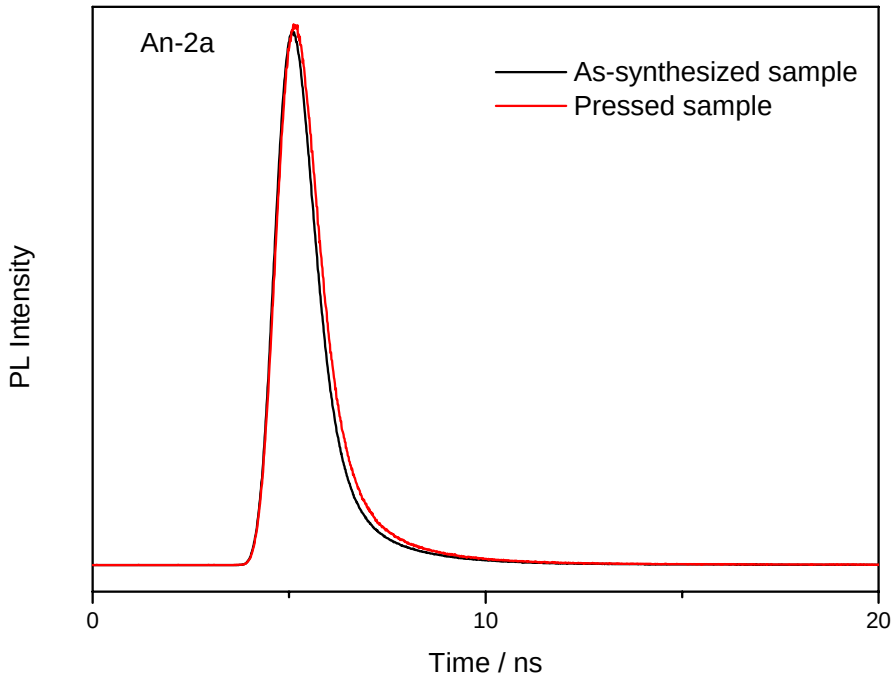


Figure S31. Time-resolved emission decay curves of An-2a.

12. Structure data of the compounds (^{1}H-NMR, ^{13}C-NMR, HRMS and FTIR)

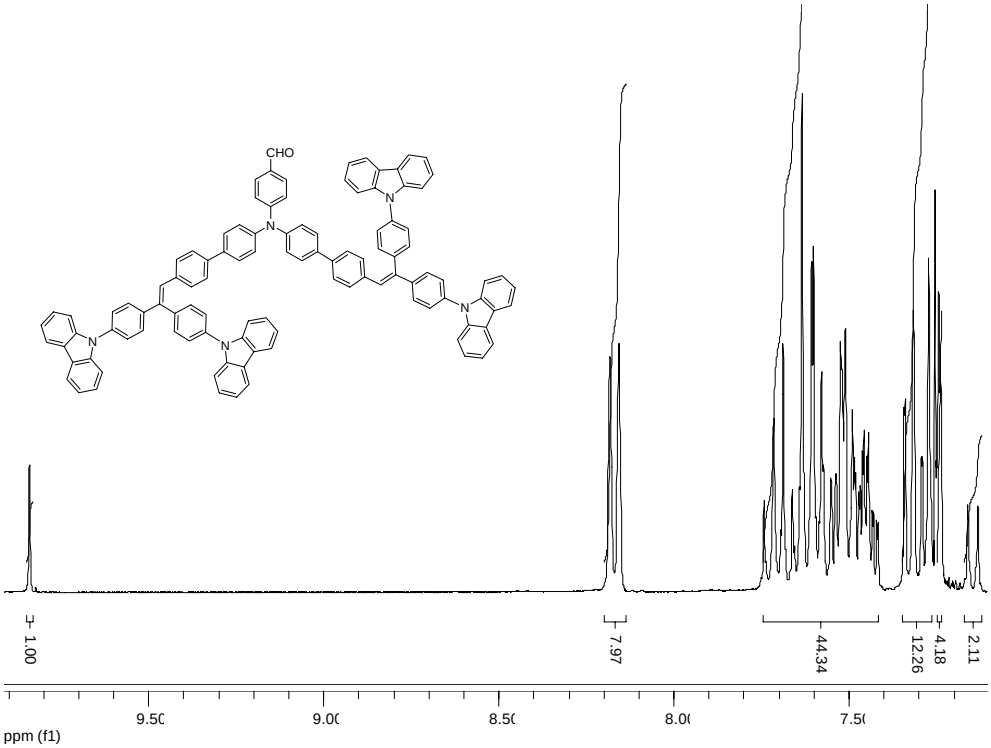


Figure S32. ^{1}H-NMR spectrum of compound **11**.

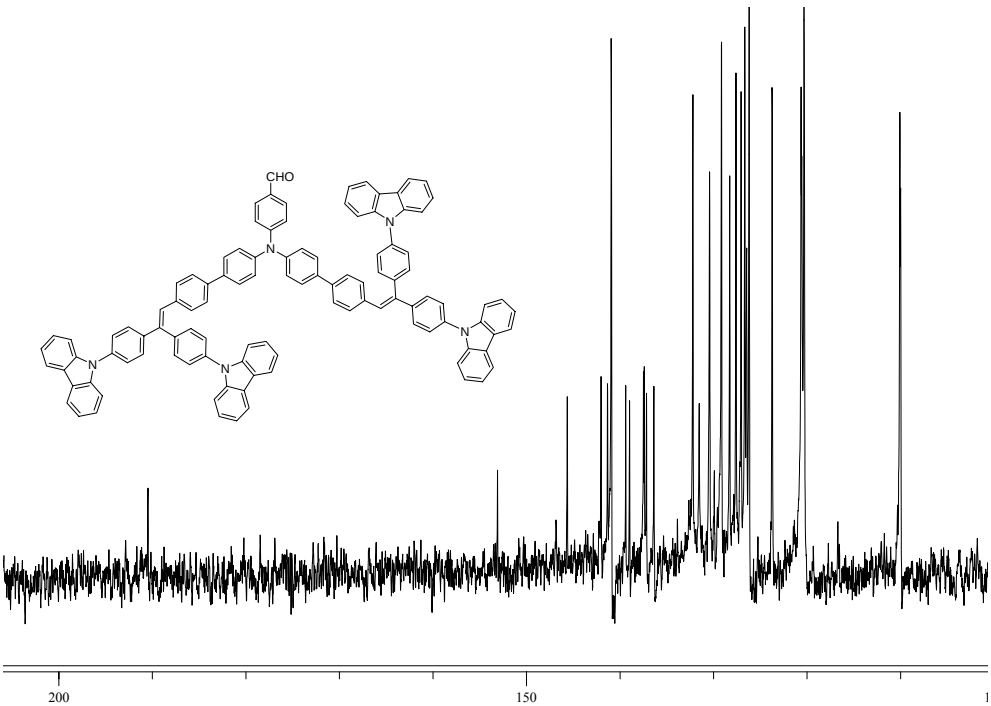


Figure S33. ^{13}C-NMR spectrum of compound **11**.

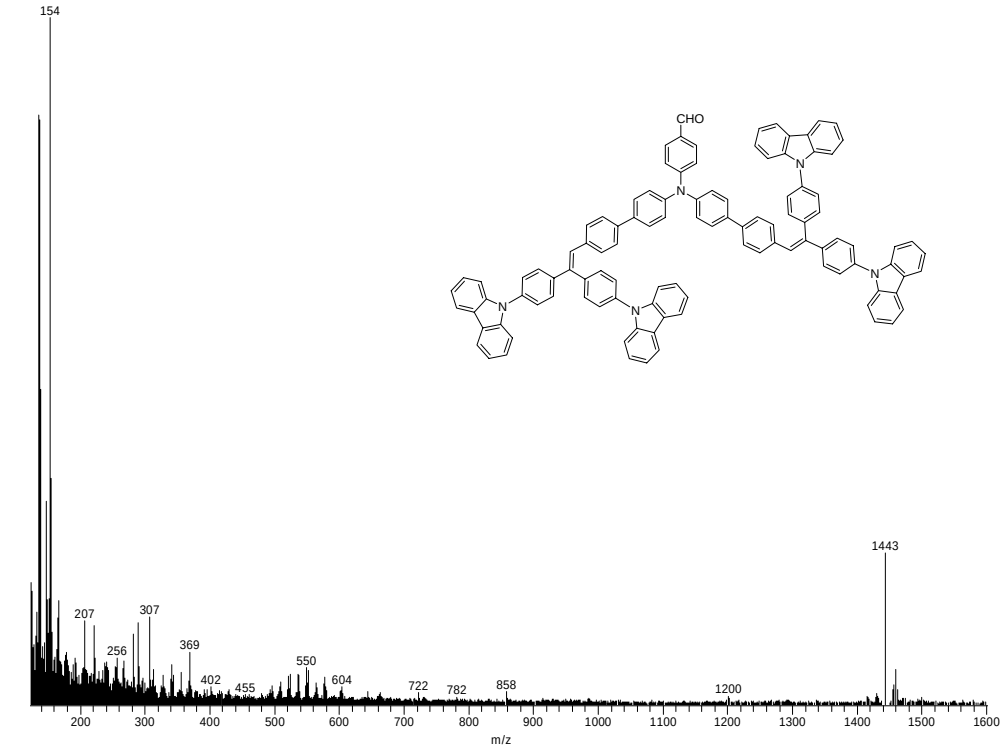


Figure S34. HRMS spectrum of compound **11**.

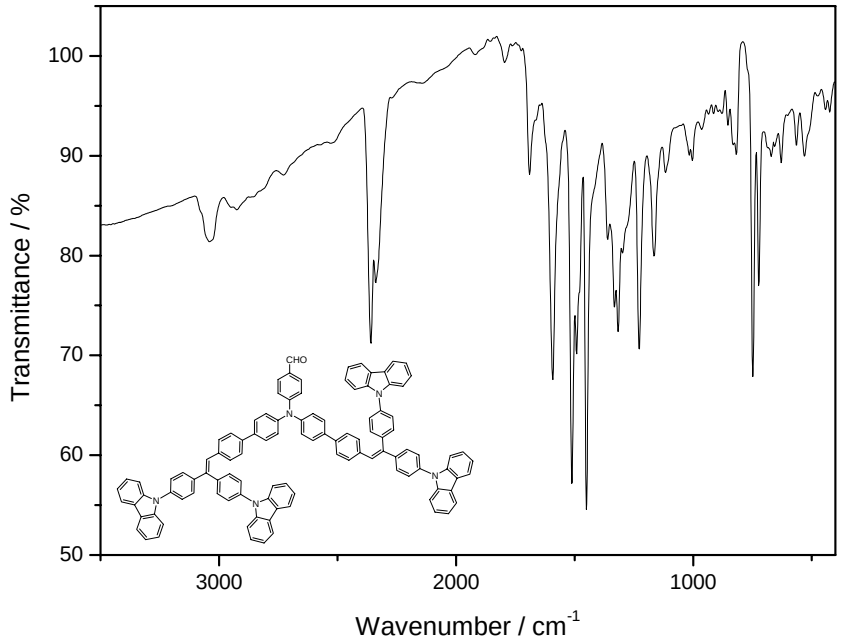


Figure S35. FT-IR spectrum of compound **11**.

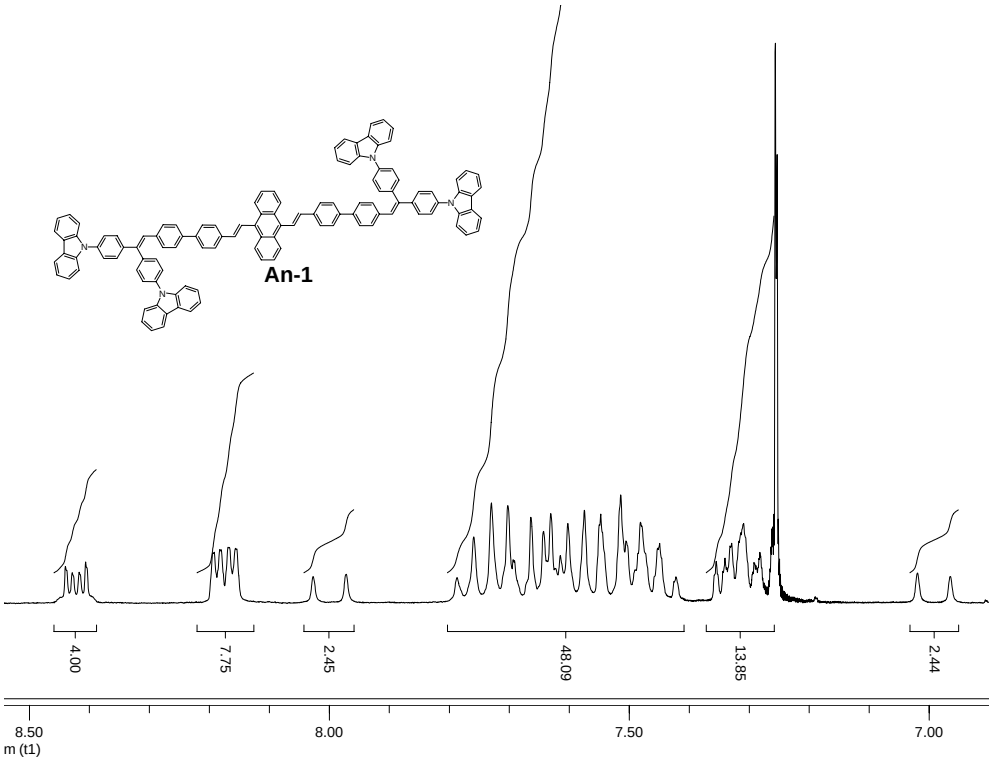


Figure S36. ^{1}H-NMR spectrum of compound **An-1**.

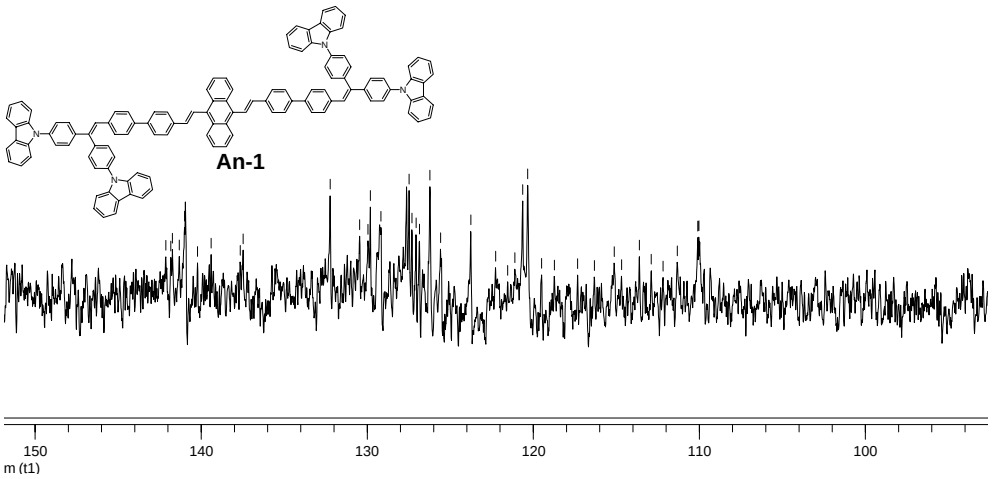


Figure S37. ^{13}C-NMR spectrum of compound **An-1**.

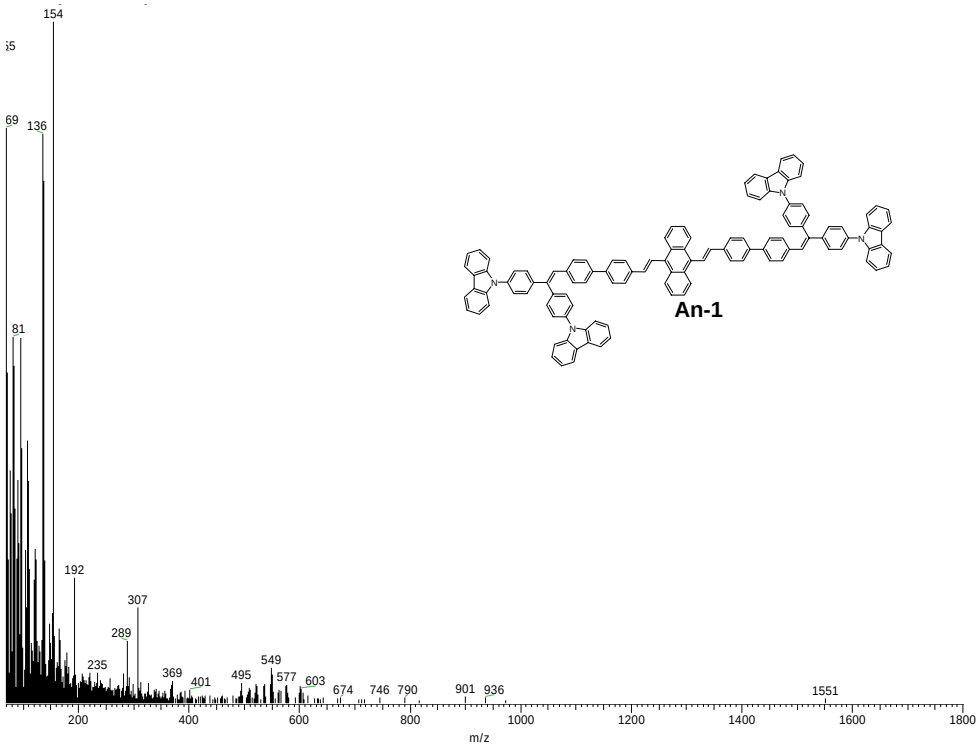


Figure S38. HRMS spectrum of compound **An-1**.

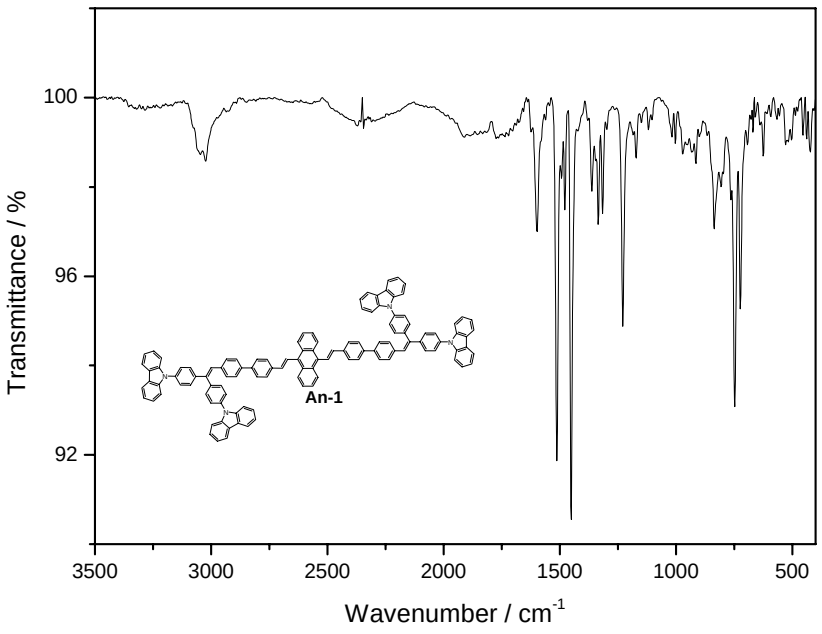


Figure S39. FT-IR spectrum of compound **An-1**.

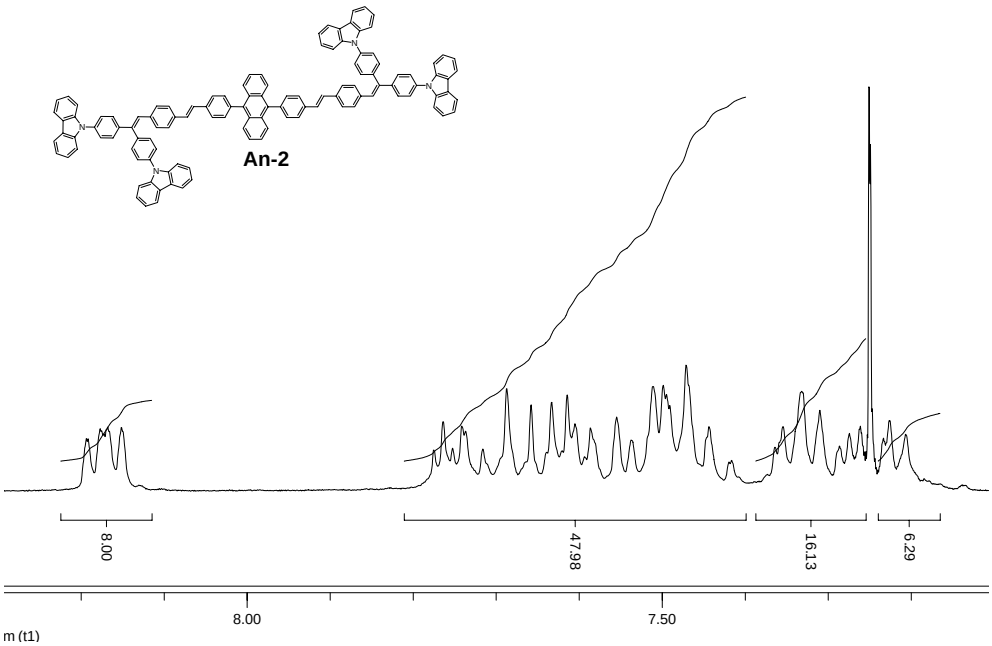


Figure S40. ^{1}H-NMR spectrum of compound **An-2**.

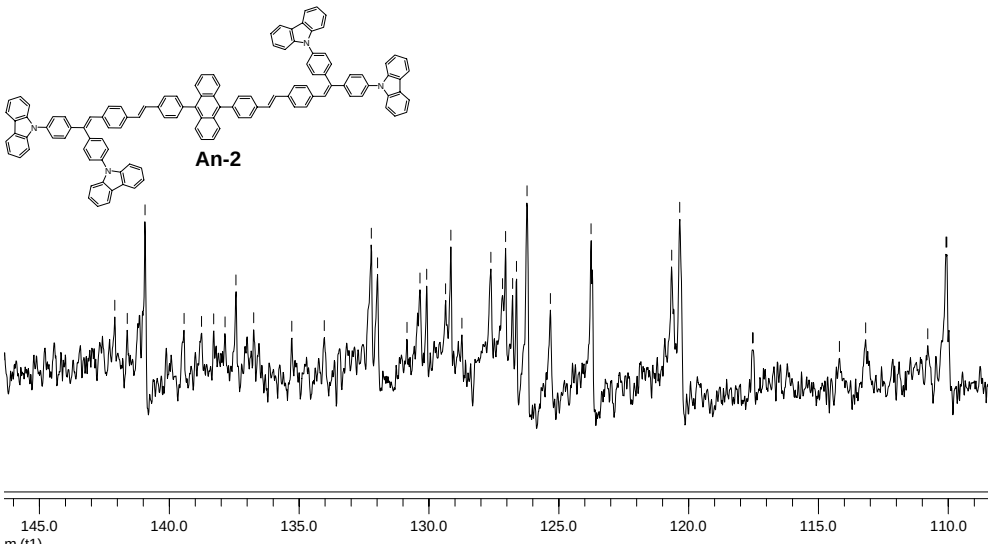


Figure S41. ^{13}C-NMR spectrum of compound **An-2**.

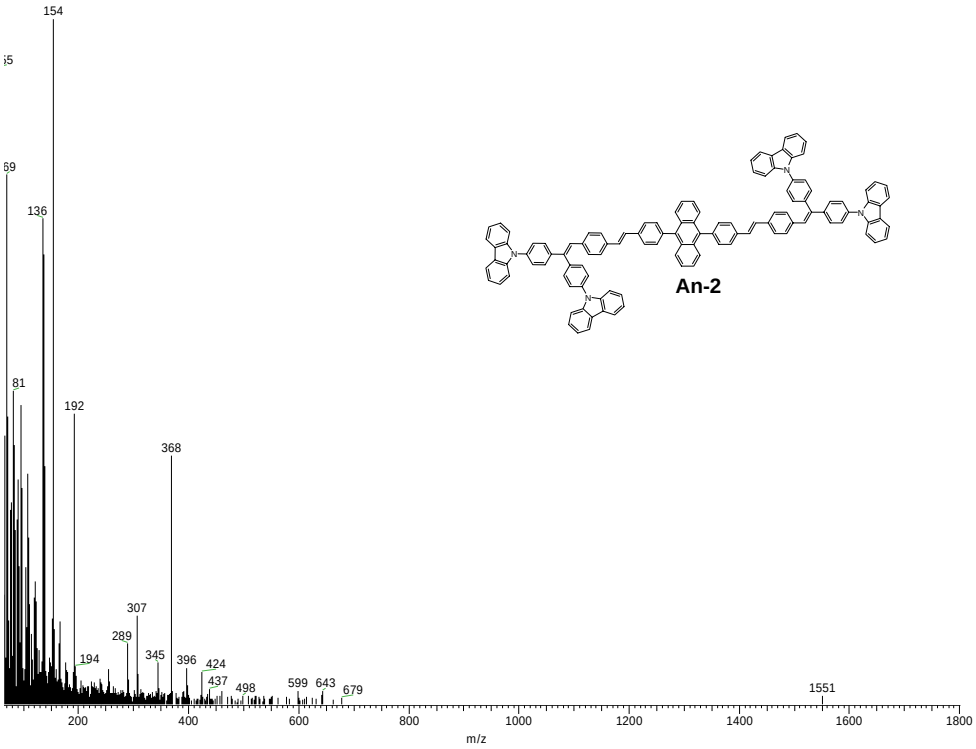


Figure S42. HRMS spectrum of compound **An-2**.

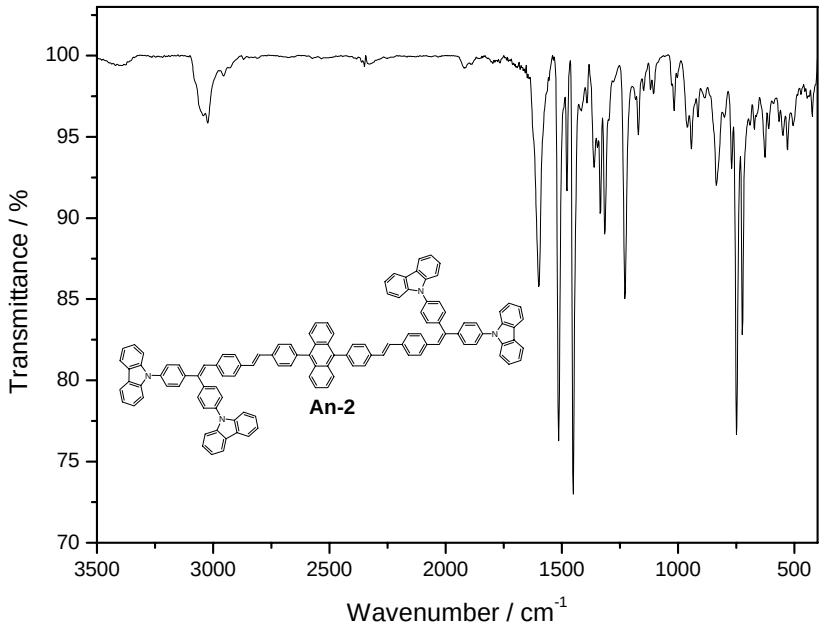


Figure S43. FT-IR spectrum of compound **An-2**.

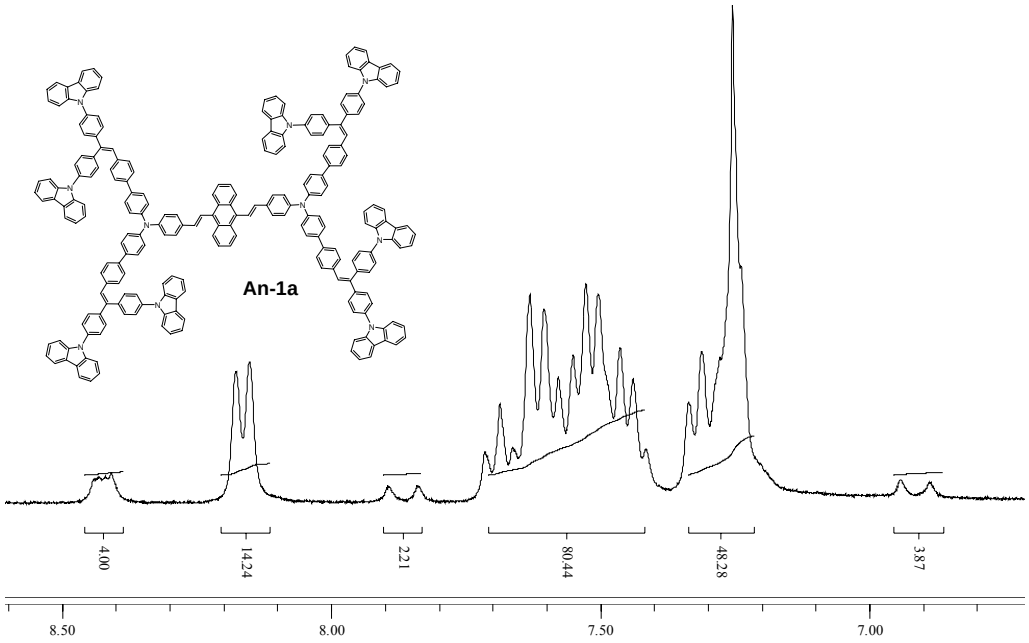


Figure S44. ^{1}H-NMR spectrum of compound **An-1a**.

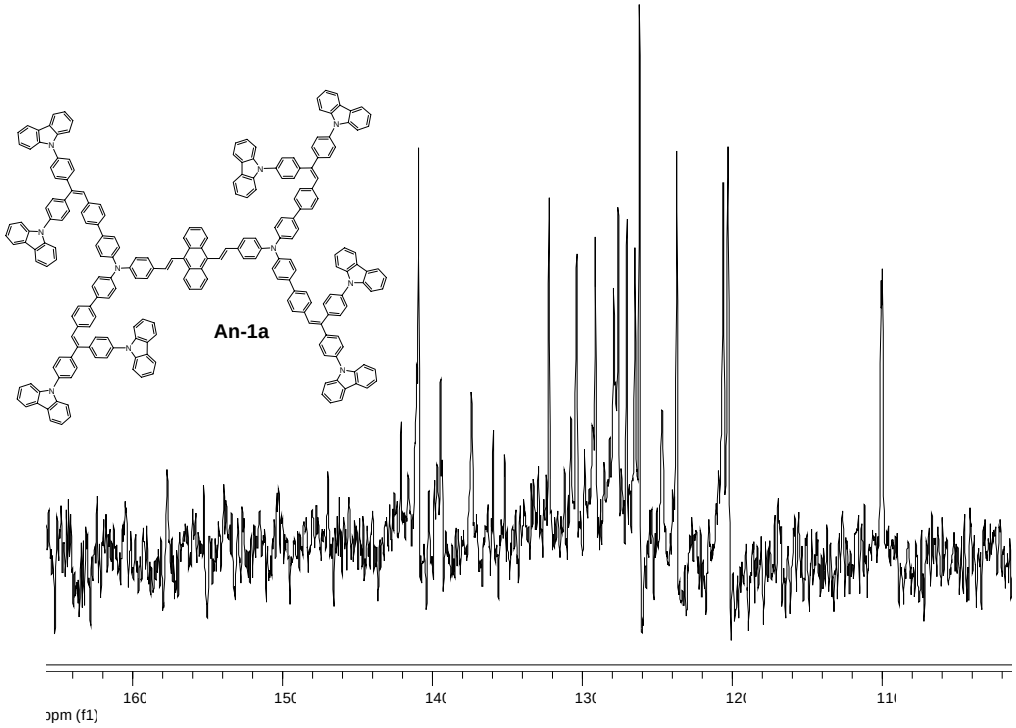


Figure S45. ^{13}C-NMR spectrum of compound **An-1a**.

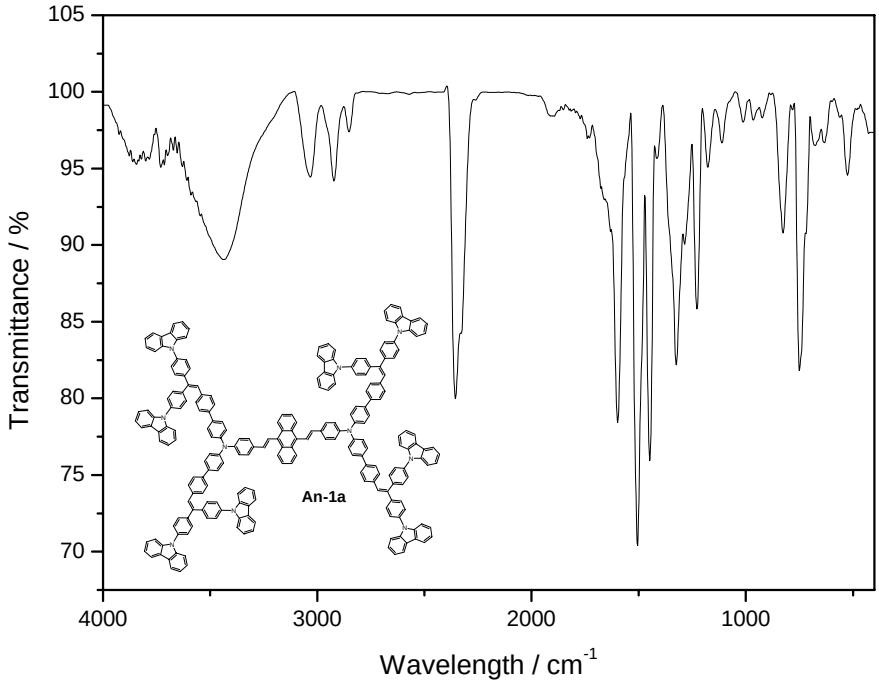


Figure S46. FT-IR spectrum of compound **An-1a**.

Note 1: a)**An-1** has low solubilty in $CDCl_3$ resulting in very weak ^{13}C-NMR signal intensity. b)The molecular weight of **An-1a** is 3055 g/mol, which is too high to detect by high resolution mass spectrometer.

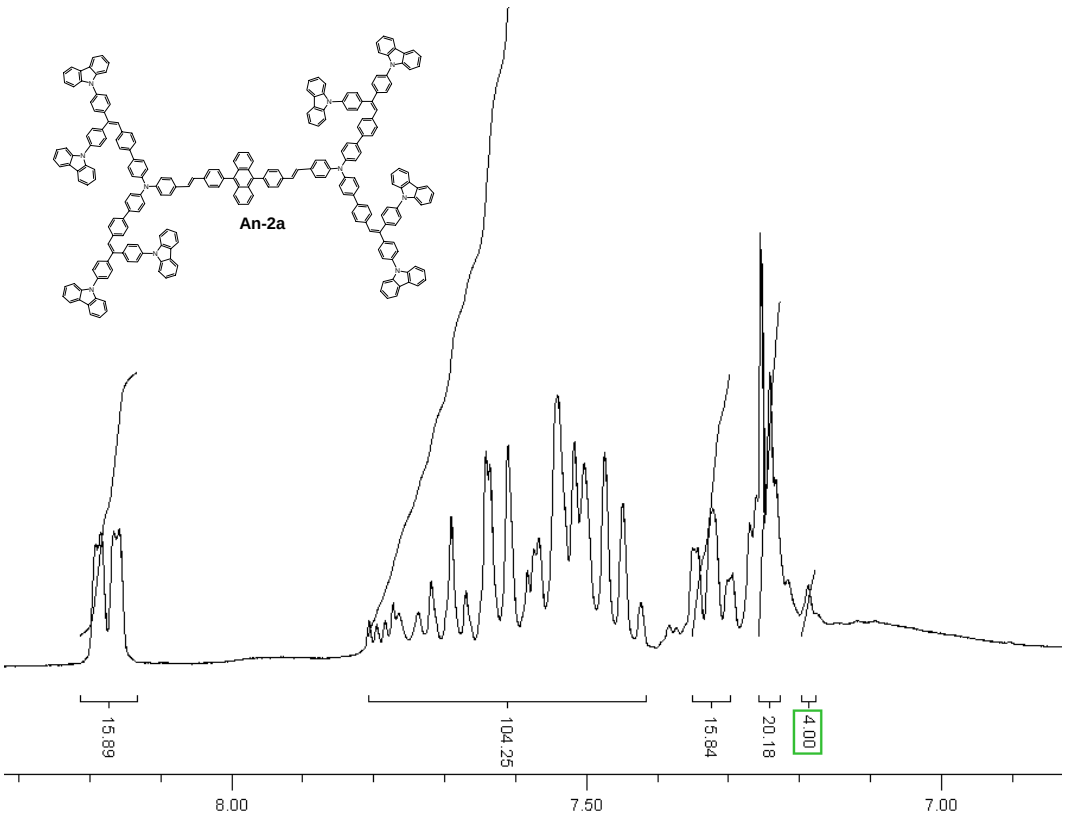


Figure S47. ^{1}H-NMR spectrum of compound **An-2a**.

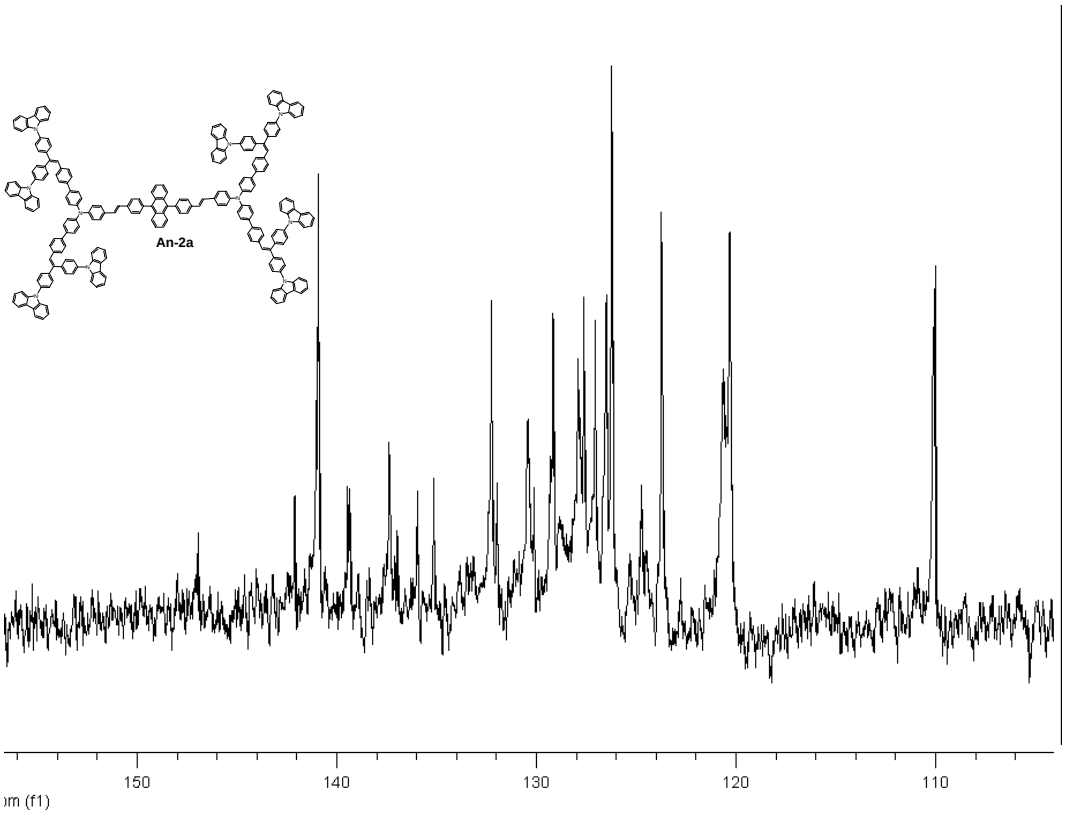


Figure S48. ^{13}C-NMR spectrum of compound **An-2a**.

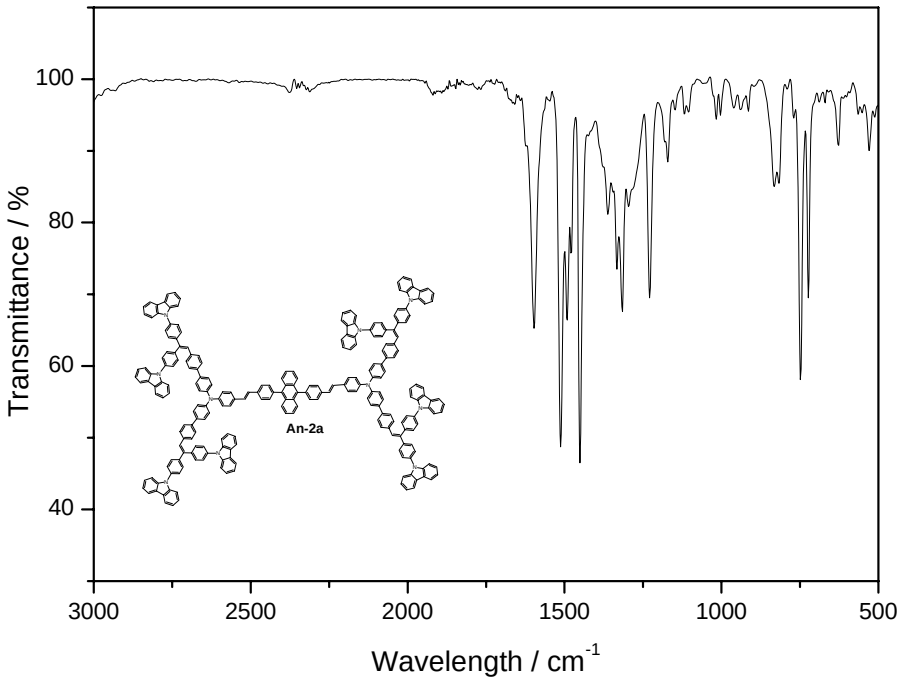


Figure S49. FT-IR spectrum of compound **An-2a**.

Note 2: The molecular weight of **An-2a** is 3208 g/mol, which is too high to detect by high resolution mass spectrometer.

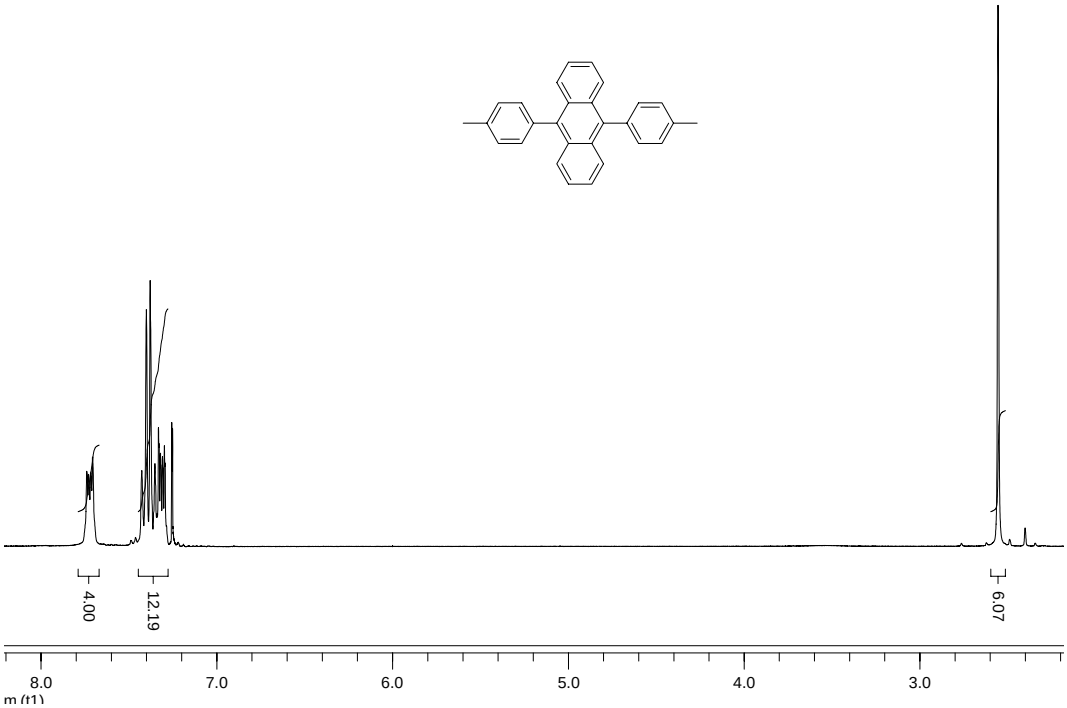


Figure S50. ^{1}H-NMR spectrum of the intermediate **2**.

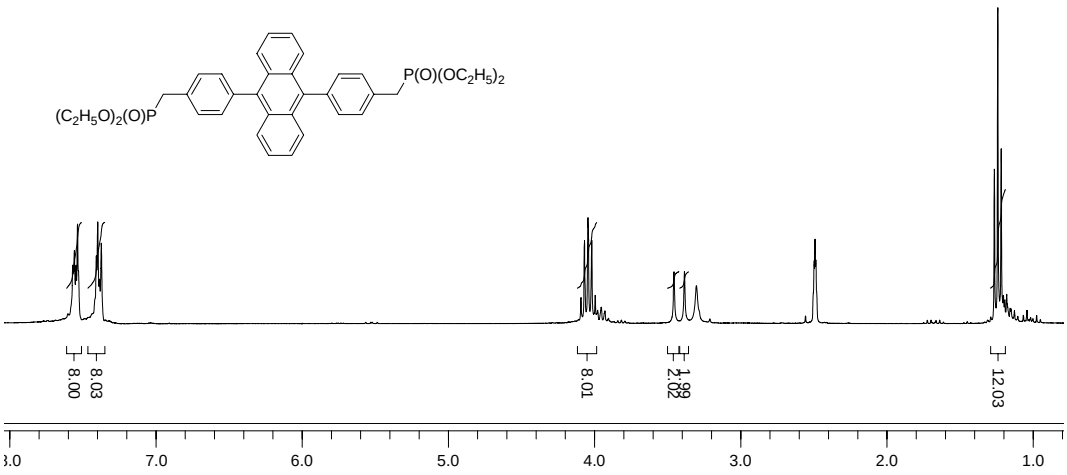


Figure S51. ^{1}H-NMR spectrum of the intermediate **3**.

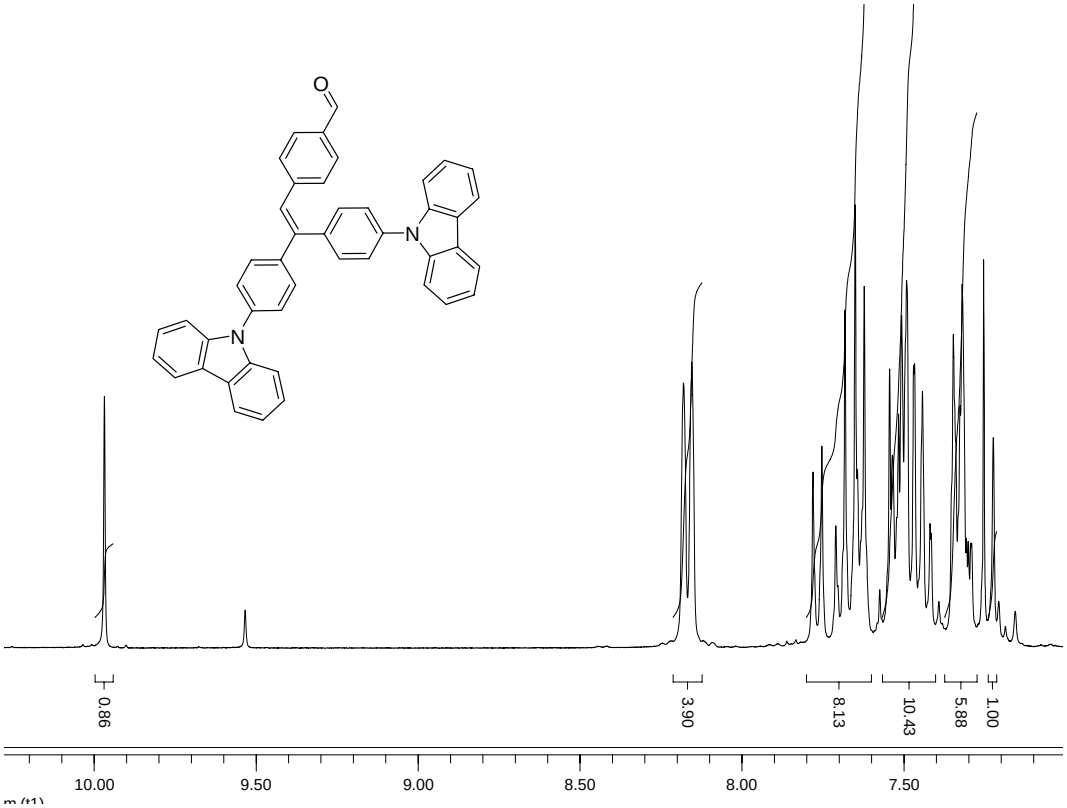


Figure S52. ^{1}H-NMR spectrum of the intermediate **9**.