Supporting Information

Imidazole-based AIEgens for highly sensitive and selective detection of picric acid

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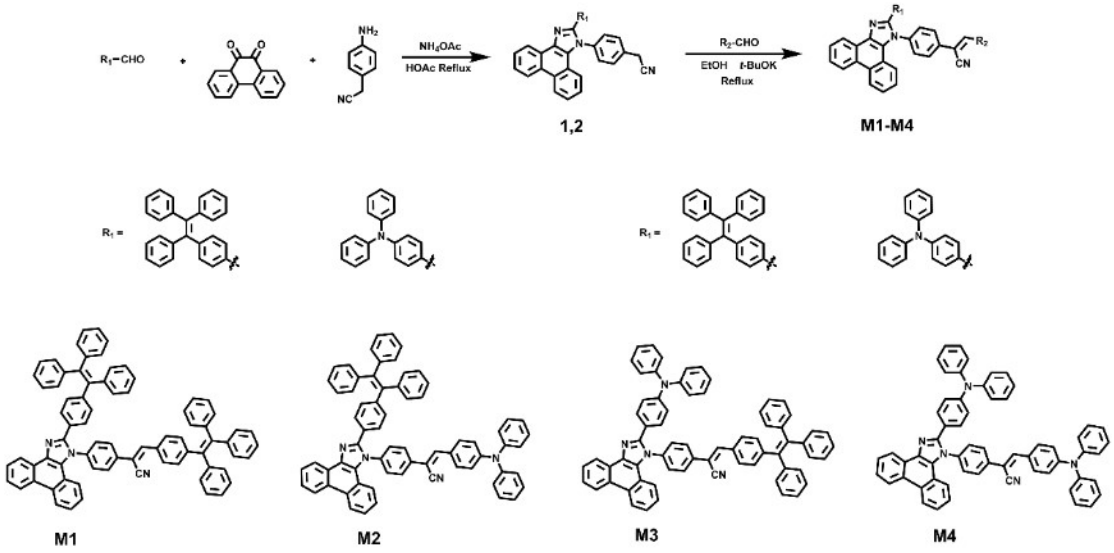
Synthesis



Scheme S1. Synthetic routes of compounds **M1**, **M2**, **M3**, and **M4**.

Synthesis of compound **1**

Phenanthrenequinone (1.00g, 4.80 mmol) and tetraphenyl monaldehyde (2.08 g, 5.76 mmol) were dissolved in anhydrous acetic acid (30 mL) at room temperature. 2-(4-Aminophenyl) acetonitrile (0.95 g, 7.20 mmol) was dissolved in glacial acetic acid (10 mL) and was gradually added into this mixture solution. The mixture was stirred for 2 h at 25 °C. Then, ammonium acetate (1.48 g, 19.21 mmol) was added and the mixture was heated to 120 °C for 12 h. The final mixture was poured into brine (200mL) and was neutralized with NaOH aqueous solution. A large amount of precipitate was filtered and washed with ethanol to afford green compound **1**(2.00 g, 3.01 mmol). Yield: 63%. FT-IR (KBr, cm^{-1}): 3053, 3022, 2920, 2251, 1611, 1514, 1447, 1148, 1022, 753, 700. ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ: 3.95 (s, 2H), 6.95-7.01 (m, 8H), 7.09-7.17 (m, 10H), 7.25-7.27 (m, 2H), 7.47-7.55 (m, 5H), 7.64 (t, *J* =7.68 Hz, 1H), 7.73 (t, *J* = 7.16 Hz, 1H), 8.69 (d, *J* = 8.20 Hz, 1H), 8.76 (d, *J* = 8.20 Hz, 1H), 8.83 (d, *J* = 8.00 Hz, 1H).

Synthesis of compound **2**

Phenanthrenequinone (1.00 g, 4.80 mmol) and tetraphenyl monaldehyde (2.08 g, 5.76 mmol) were dissolved in anhydrous acetic acid (30 mL) at room temperature. 2-(4-Aminophenyl) acetonitrile (0.95 g, 7.20 mmol), was dissolved in glacial acetic acid

(10 mL) and was gradually added into this mixture solution. The mixture was stirred for 2 h at 25 °C. Then, ammonium acetate (1.48 g, 19.21 mmol) was added and the mixture was heated to 120 °C for 12 h. The final mixture was poured into brine (200 mL) and was neutralized with NaOH aqueous solution. A large amount of precipitate was filtered and washed with ethanol to afford green compound **1** (2.00 g, 3.47 mmol). Yield: 72%. FT-IR (KBr, cm^{-1}): 3058, 3035, 2244, 1588, 1515, 1445, 1325, 1270, 1171, 758, 694. ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ: 3.74 (s, 2H), 6.90 (d, *J* = 8.72 Hz, 2H), 7.06-7.11 (m, 10H), 7.24-7.32 (m, 14H), 7.63 (d, *J* = 7.80 Hz, 2H).

Synthesis of compound **M1**

Compound **1** (0.3g, 0.45 mmol) and TPE-CHO (0.17g, 0.47mmol) were uniformly dispersed in ethanol (20 mL) at 80 °C. Soon afterwards, *t*-BuOK (0.10 g, 0.90 mmol) was added. The reaction mixture was refluxed for 4 h. The final mixture was poured into brine (200 mL). The generated green precipitate was filtered and further purified by column chromatography (petroleum ether: ethyl acetate = 4:1, v/v) to afford compound **M1** (0.37 g, 0.37 mmol). Yield: 81%. FT-IR (KBr, cm^{-1}): 3052, 30234, 2923, 2849, 2215, 1598, 1513, 1444, 1186, 853, 752, 672. ^1H NMR ($CDCl_3$, 400 MHz, ppm) δ: 6.95-7.27 (m, 3H), 7.59 (s, 1H), 7.64 (d, *J* = 7.70 Hz, 1H), 7.71-7.76 (m, 3H), 7.82 (d, *J* = 7.70 Hz, 2H), 8.69 (d, *J* = 8.40 Hz, 1H), 8.76 (d, *J* = 8.40 Hz, 1H), 8.83 (d, *J* = 7.92 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm) δ: 117.85, 120.74, 122.79, 122.83, 123.12, 124.23, 125.01, 125.73, 126.39, 126.62, 126.84, 127.00, 127.11, 127.22, 127.35, 127.68, 127.73, 127.68, 127.73, 127.89, 127.94, 128.09, 128.29, 128.74, 129.03, 129.30, 129.75, 131.23, 131.30, 131.37, 131.44, 132.12, 135.83, 137.60, 139.13, 139.93, 140.16, 141.74, 142.72, 143.08, 143.26, 143.37, 143.44, 143.50, 144.61, 147.28, 150.92. HR-MS (APCI-MS): m/z [$(M+H)^+$] calcd : 1006.4083, found = 1006.4161.

Synthesis of compound **M2**

Compound **1** (0.20 g, 0.30 mmol) and TPA-CHO (0.91 g, 0.33 mmol) were uniformly dispersed in ethanol (20 mL) at 80 °C. Soon afterwards, *t*-BuOK (0.068 g, 0.60 mmol) was added. The reaction mixture was refluxed for 4 h. The final mixture was poured into brine (100 mL). The generated green precipitate was filtered and

further purified by column chromatography (petroleum ether: ethyl acetate = 4:1, v/v) to afford compound **M2** (0.20 g, 0.22 mmol). Yield: 72%. FT-IR (KBr, cm^{-1}): 3055, 3024, 2922, 2849, 2214, 1592, 1489, 1445, 1279, 1028, 751, 698. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 6.82 (d, *J* = 8.88 Hz, 1H), 6.90-7.21 (m, 27H), 7.24-7.39 (m, 8H), 7.43-7.51 (m, 2H), 7.60-7.66 (m, 2H), 7.70-7.74(m, 1H), 7.81-7.88 (m, 2H), 8.68-8.70 (m, 1H), 8.73-8.77 (m, 1H), 8.81-8.84 (m, 1H). ^{13}C NMR ($CHCl_3$, 100 MHz, ppm) δ: 109.31, 117.96, 120.72, 121.96, 122.90, 122.99, 123.19, 123.37, 123.69, 124.31, 124.93, 125.23, 125.73, 126.46, 126.90, 127.07, 127.38, 127.22, 127.49, 127.81, 127.97, 128.02, 128.34, 129.13, 129.28, 129.47, 129.96, 130.20, 131.32, 131.38, 131.45, 132.16, 136.08, 137.69, 139.50, 140.01, 143.17, 142.77, 143.34, 143.52, 147.24, 147.32, 148.63, 150.98. HR-MS (APCI-MS): m/z [$(M+H)^+$] calcd : 919.3722, found = 919.3813.

Synthesis of compound **M3**

Compound **2** (0.15 g, 0.23 mmol) and TPE-CHO (0.068 g, 0.25 mmol) were uniformly dispersed in ethanol (20 mL) at 80 °C. Soon afterwards, *t*-BuOK (0.051 g, 0.45 mmol) was added. The reaction mixture was refluxed for 4 h. The final mixture was poured into brine (100 mL). The generated green precipitate was filtered and further purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1, v/v) to afford compound **M3** (0.15 g, 0.16 mmol). Yield: 72%. FT-IR (KBr, cm^{-1}): 3055, 3024, 2922, 2849, 2214, 1592, 1489, 1445, 1279, 1028, 751, 698. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 6.95-7.29 (m, 33H), 7.49-7.53 (m, 3H), 7.59 (s, 1H), 7.64 (t, *J* = 7.72 Hz, 1H), 7.71-7.76 (m, 3H), 7.82 (d, *J* = 7.68 Hz, 2H), 8.69 (d, *J* = 8.24 Hz, 1H), 8.76 (d, *J* = 8.44 Hz, 1H), 8.83 (d, *J* = 7.92 Hz, 1H). ^{13}C NMR ($CHCl_3$, 100 MHz, ppm) δ: 109.15, 120.06, 120.67, 122.89, 123.17, 124.28, 124.79, 125.03, 125.29, 125.81, 125.96, 1226.10, 126.25, 126.72, 127.44, 127.74, 127.81, 127.89, 128.08, 128.33, 128.84, 129.38, 129.76, 129.97, 130.81, 131.39, 131.43, 131.49, 135.03, 137.71, 139.20, 140.21, 141.82, 143.23, 143.51, 144.85, 145.46, 146.37, 150.23, 151.03. HR-MS (APCI-MS): m/z [$(M+H)^+$] calcd : = 918.3722, found = 918.3828.

Synthesis of compound **M4**

Compound **2** (0.20 g, 0.35 mmol) and TPA-CHO (0.10 g, 0.38 mmol) were uniformly dispersed in ethanol (20 mL) at 80 °C. Soon afterwards, *t*-BuOK (0.078 g, 0.38 mmol) was added. The reaction mixture was refluxed for 4 h. The final mixture was poured into brine (100 mL). The generated green precipitate was filtered and further purified by column chromatography (petroleum ether : ethyl acetate = 4 : 1, v/v) to afford compound **M4** (0.20 g, 0.24 mmol). Yield: 69%. FT-IR (KBr, cm^{-1}): 3058, 3034, 2921, 2847, 2365, 2198, 1589, 1489, 1332, 1279, 1195, 1074, 828, 749, 692, 508. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 6.96 (d, *J* = 8.84 Hz, 2H), 7.02-7.36 (m, 24H), 7.44 (d, *J* = 8.84 Hz, 2H), 7.51 (t, *J* = 8.24 Hz, 1H), 7.59 (d, *J* = 8.24 Hz, 3H), 7.65 (t, *J* = 8.36 Hz, 1H), 7.73 (d, *J* = 7.08 Hz, 1H), 7.85 (q, *J* = 8.60 Hz, 4H), 8.70 (t, *J* = 8.28 Hz, 1H), 8.77 (d, *J* = 8.32 Hz, 1H), 8.86 (d, *J* = 8.00 Hz, 1H). ^{13}C NMR ($CHCl_3$, 100 MHz, ppm) δ: 106.05, 118.66, 120.29, 120.50, 120.77, 121.97, 122.91, 123.03, 123.19, 123.69, 124.28, 124.72, 124.83, 124.92, 125.18, 125.23, 125.71, 125.84, 125.90, 126.07, 126.48, 127.21, 127.37, 128.01, 128.35, 129.26, 129.48, 129.76, 129.85, 130.22, 131.13, 136.53, 137.61, 138.92, 143.25, 146.50, 147.25, 148.62, 150.62, 150.99. HR-MS (APCI-MS): m/z [$(M+H)^+$] calcd : 832.3362, found = 832.3439.

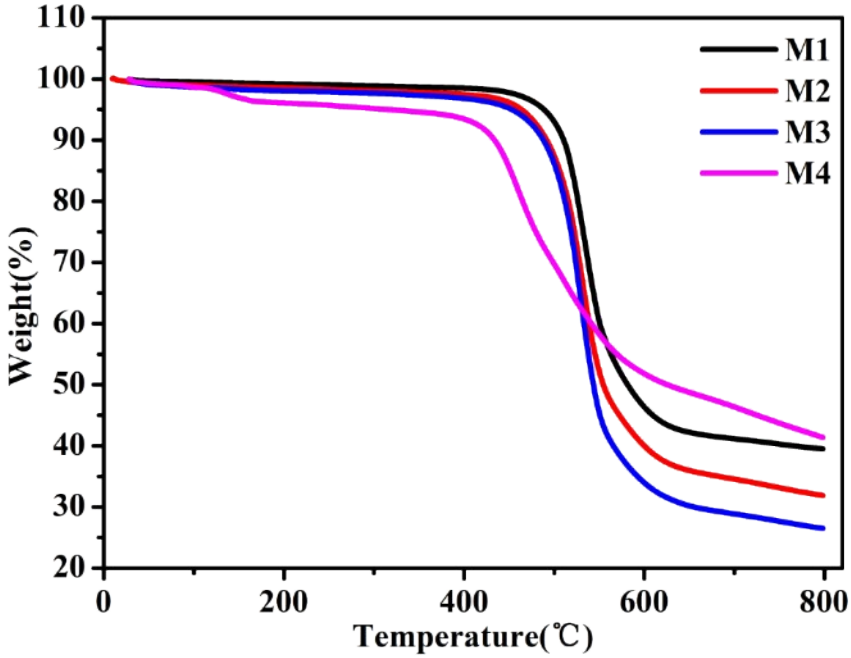


Fig. S1. The TGA curve of compounds **M1**, **M2**, **M3**, and **M4**.

Table S1 Summary of crystallographic data and structure refinement details for **M3**.

Identification code	**M3**	Volume	5791.5(2) Å^3
Empirical formula	$C_{68}H_{46}N_4$	Z, Calculated density	4, 1.054 g cm^{-3}
Formula weight	919.09	Absorption coefficient	0.472 mm^{-1}
Temperature	273.15 K	*F*(000)	1928.0
Wavelength	1.54178 Å	2θ range for data collection	4.128 to 137.984°
Crystal system	monoclinic		$-25 \le h \le 25$
Space group	P-2_1/C	Index ranges	$-33 \le k \le 33$
a	21.4031(5) Å		$-11 \le l \le 10$
b	27.8054(6) Å	Data/restraints/parameters	10684/1/650
c	9.7334(2) Å	Goodness-of-fit on F^2	0.991
α	90°	Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0763$, $wR_2 = 0.2052$
β	91.110(2)°	Final *R* indices (all data)	$R_1 = 0.1259$, $wR_2 = 0.2524$
		Reflections collected	109458
γ	90°	Independent reflections	10684 [$R_{int} = 0.1167$, $R_{sigma} = 0.0494$]

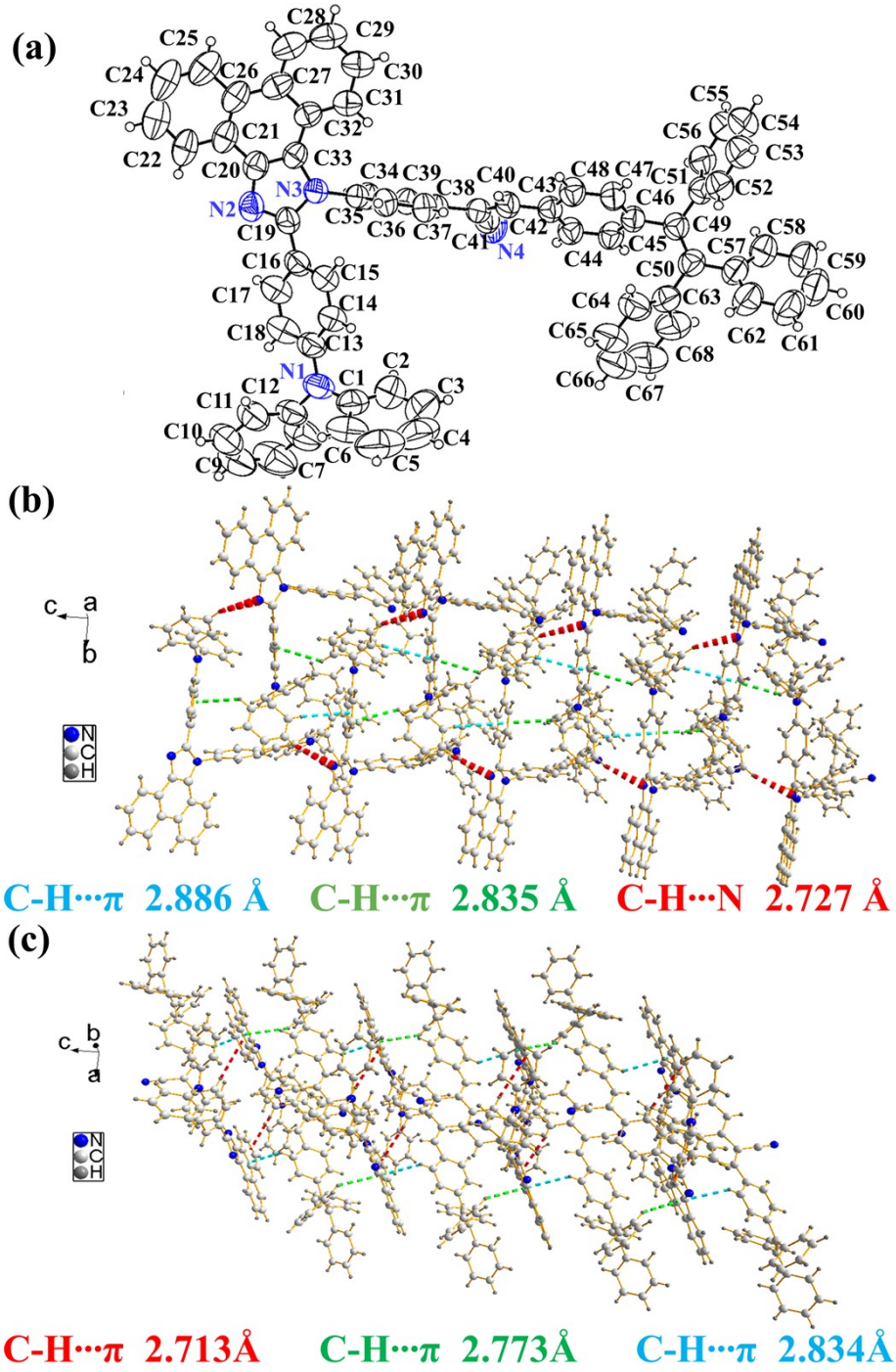


Fig. S2. The weak interactions in the single crystal of **M3**.

Table S2 A summary of weak interactions of compound **M3** in its crystalline phase.

Compound	Intermolecular Interactions	Selected bond distances/[Å]
M3	C9-H9···N2	2.727
	C8-H8···π	2.886
	C12-H12···π	2.835
	C48-H48···π	2.834
	C56-H56···π	2.713
		2.773

Table S3 The linear optical parameters of compounds **M1**, **M2**, **M3**, and **M4** in different solvents.

Compounds	Solvents	λ_{max}[a]	λ_{max}[b]	ε ($\times 10^4$)[c]	$\Delta\nu$/cm^{-1} [d]	Φ[e]
M1	benzene	368	503	5.27	7293	0.61
	DCM	367	518	4.63	7943	
	THF	367	511	4.74	7679	
	EA	363	509	4.48	7902	
	EtOH	362	503	3.69	7744	
	acetonitrile	362	497	3.63	7504	
	DMF	365	515	3.90	7980	
M2	benzene	369	506	3.84	7337	0.08
	DCM	368	526	3.59	8163	
	THF	369	518	4.15	7795	
	EA	367	519	3.74	7980	
	EtOH	364	524	3.17	8389	
	acetonitrile	364	537	3.40	8851	
	DMF	369	541	3.33	8616	
M3	benzene	369	543	4.72	8684	0.15
	DCM	367	431	4.82	4046	
	THF	369	405	5.27	2489	
	EA	364	520	5.07	8242	
	EtOH	363	430	4.47	4292	
	acetonitrile	360	426	4.71	4304	
	DMF	367	436	4.28	4312	
M4	benzene	370	423	3.80	3386	0.12
	DCM	369	425	3.63	3571	
	THF	369	421	4.19	3347	
	EA	366	420	3.76	3513	
	EtOH	363	427	3.22	4184	
	acetonitrile	364	428	3.39	4108	
	DMF	369	428	3.36	3736	

[a] Peak position of the longest absorption band. [b] Peak position of fluorescence emission, excited at the absorption maximum. [c] Molar absorptivity (L/cm/mol). [d] Stokes' shift in cm^{-1}. [e] Quantum yields in solid state

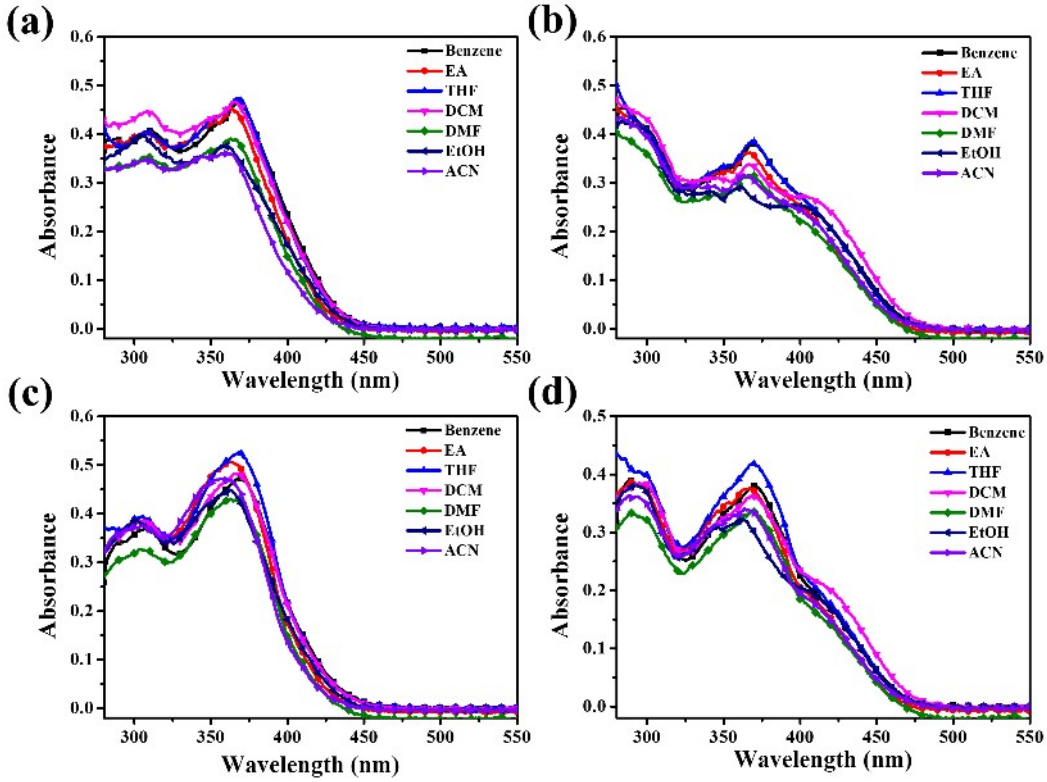


Fig. S3. UV-vis spectra of compounds (a) **M1**, (b) **M2**, (c) **M3**, and (d) **M4** in different solvents (10 μM).

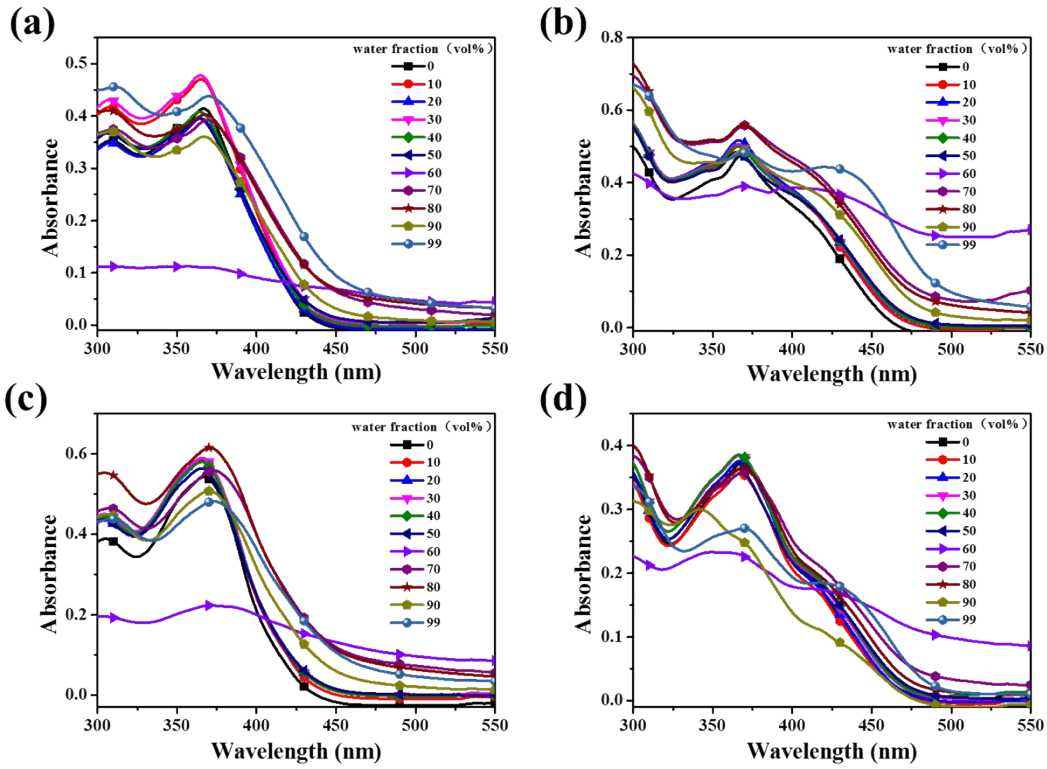


Fig. S4. UV-vis spectra of (a) **M1**, (b) **M2**, (c) **M3**, and (d) **M4** at 10 μM in THF/H_2O mixtures with different water fractions.

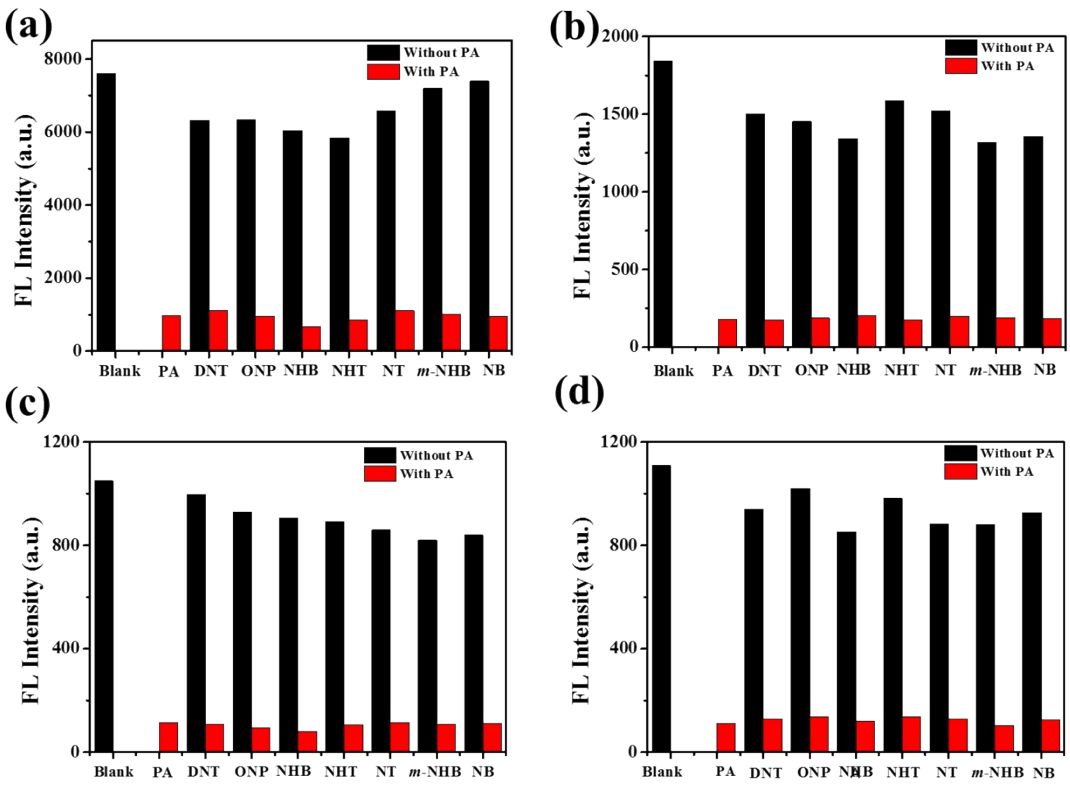


Fig. S5. Quenching percentages of compounds (a) **M1**, (b) **M2**, (c) **M3**, and (d) **M4** (10 μM) with different NACs (15 equiv.) in THF/H_2O (1/ 99, v/v) mixtures before (black) and after (red) the addition of PA (15 equiv.).

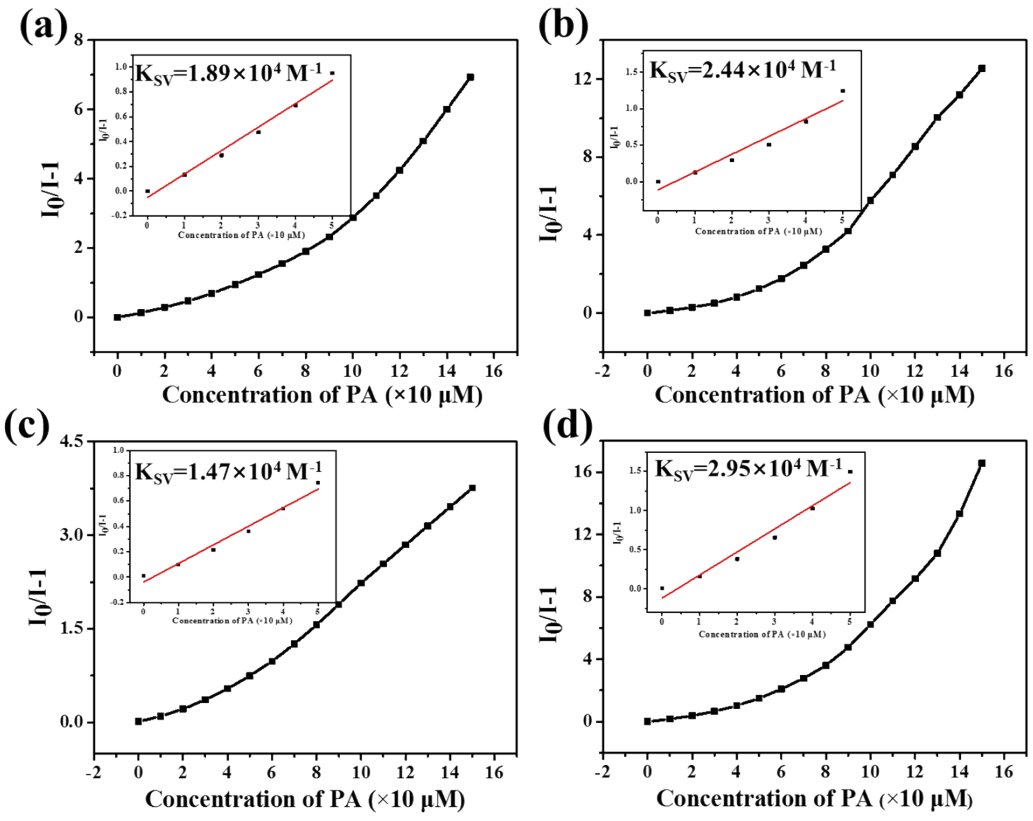


Fig. S6. Stern-Volmer plot of (a) **M1**, (b) **M2**, (c) **M3**, and (d) **M4** in response to PA.

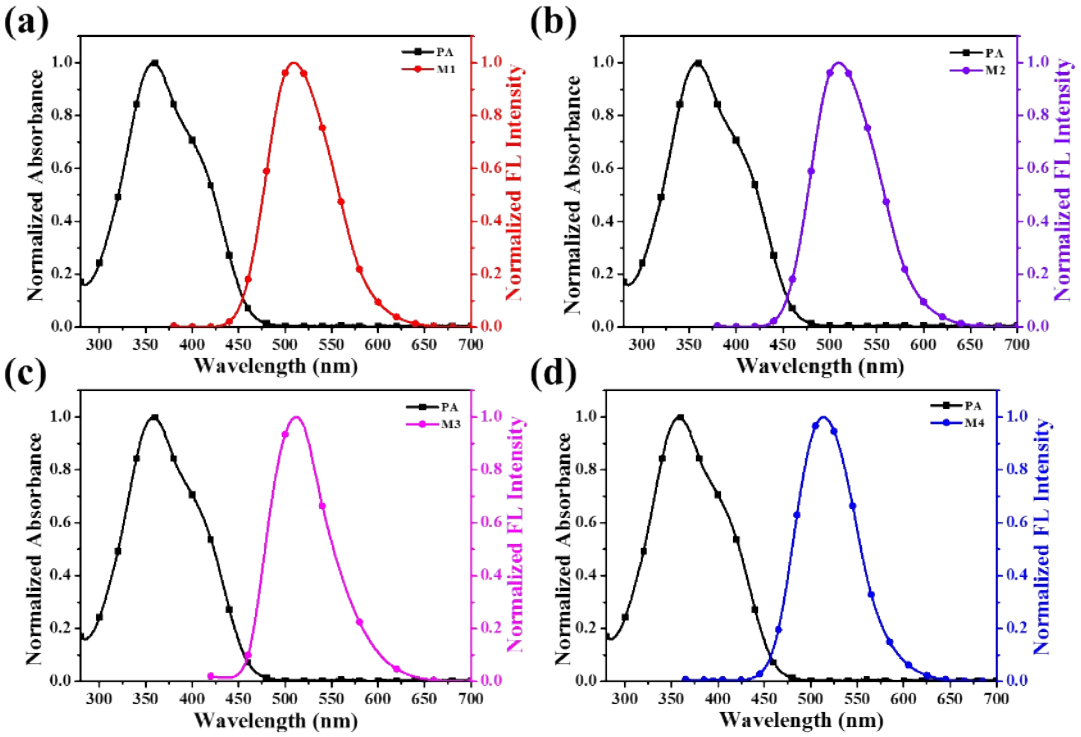


Fig. S7. Normalized UV-vis absorption spectra of PA and normalized fluorescence of (a) **M1**, (b) **M2**, (c) **M3**, and (d) **M4**.

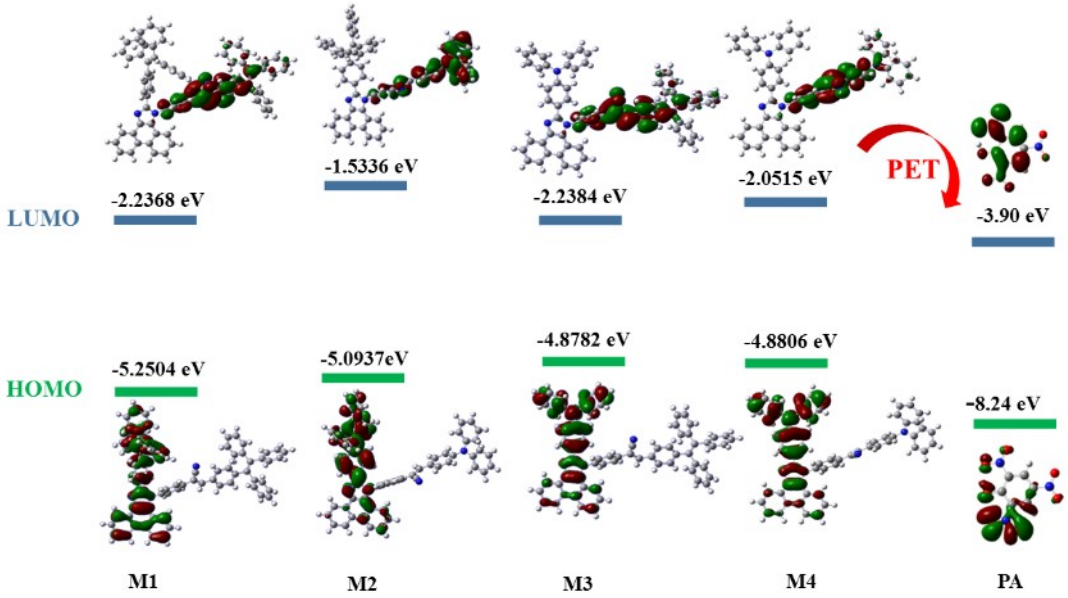


Fig. S8. Optimized molecular structures and molecular orbital amplitude plots of the LUMO and HOMO levels, energy gaps and electron cloud distribution of **M1**, **M2**, **M3**, **M4**, and PA calculated using the B3LYP/6-31G* basis set.

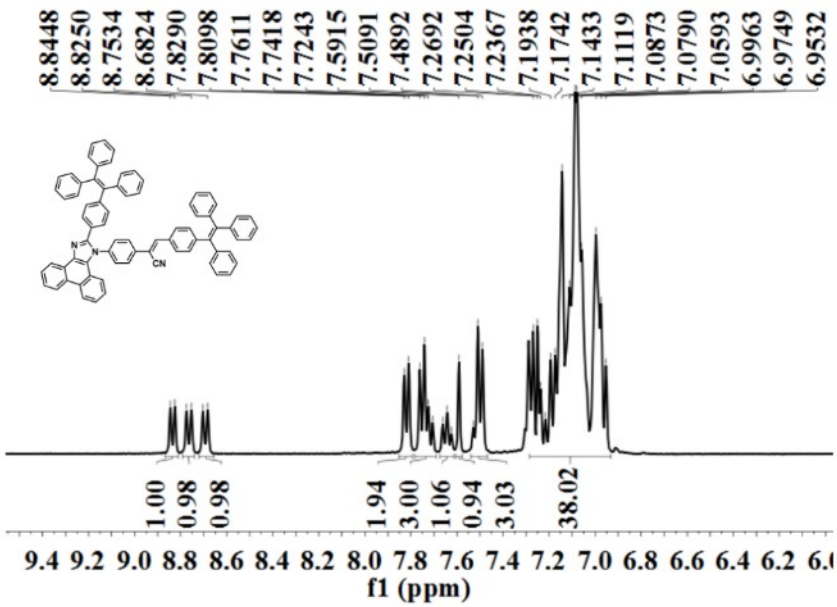


Fig. S9. ^{1}H NMR spectrum of compound **M1** in $CDCl_3$.

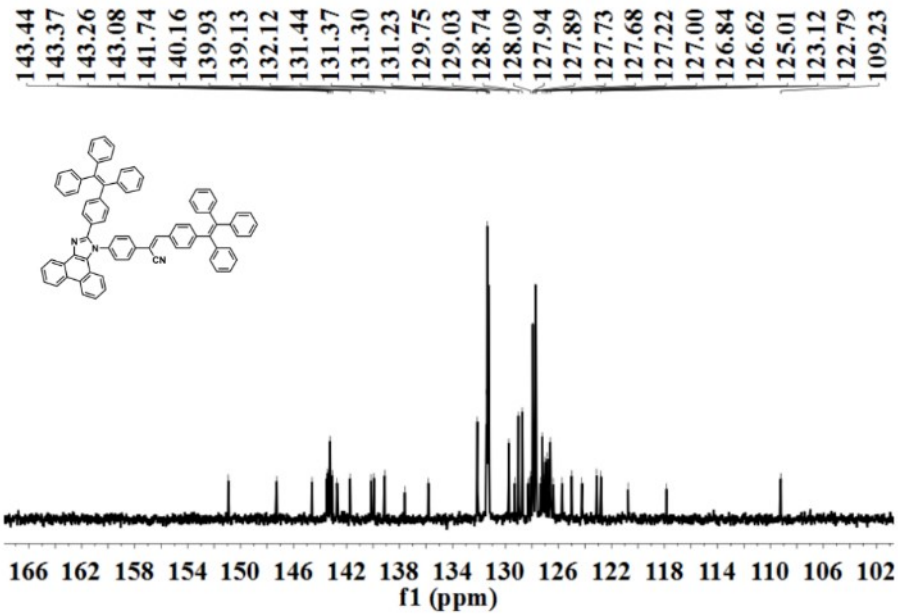


Fig. S10. ^{13}C NMR spectrum of compound **M1** in $CDCl_3$.

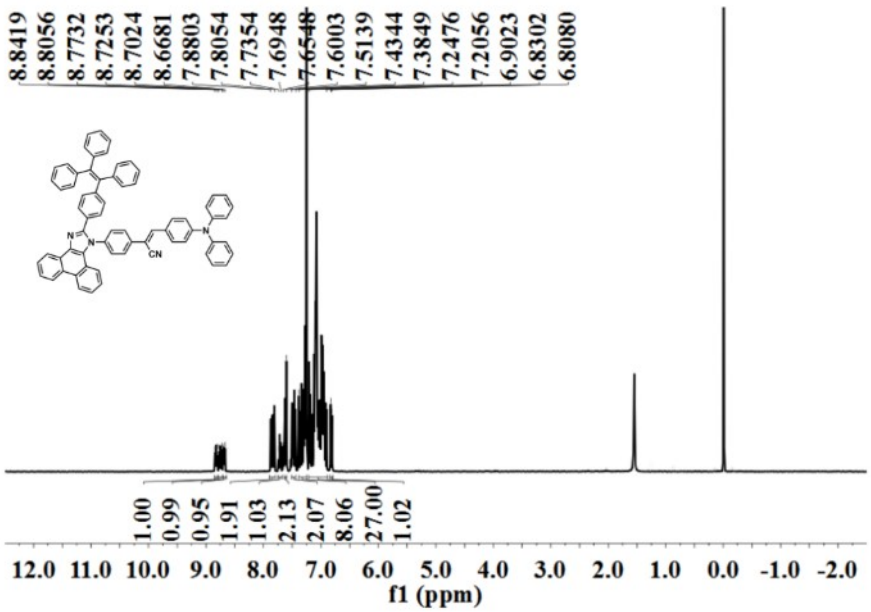


Fig. S11. ^{1}H NMR spectrum of compound **M2** in $CDCl_3$.

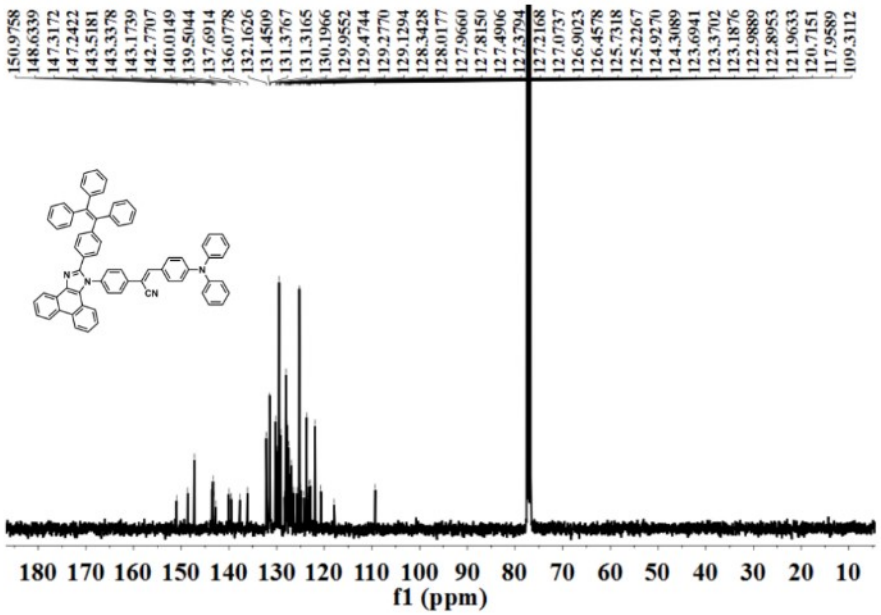


Fig. S12. ^{13}C NMR spectrum of compound **M2** in $CDCl_3$.

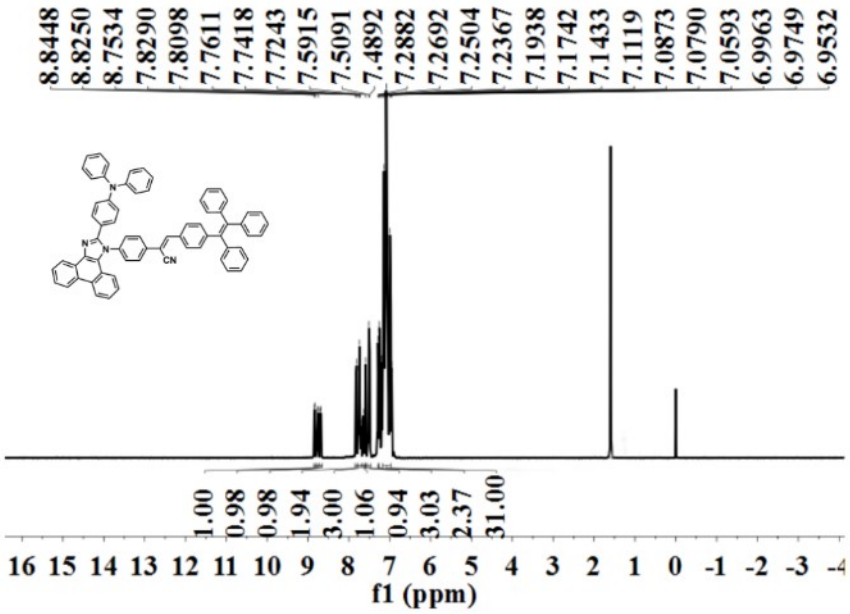


Fig. S13. ^{1}H NMR spectrum of compound **M3** in $CDCl_3$.

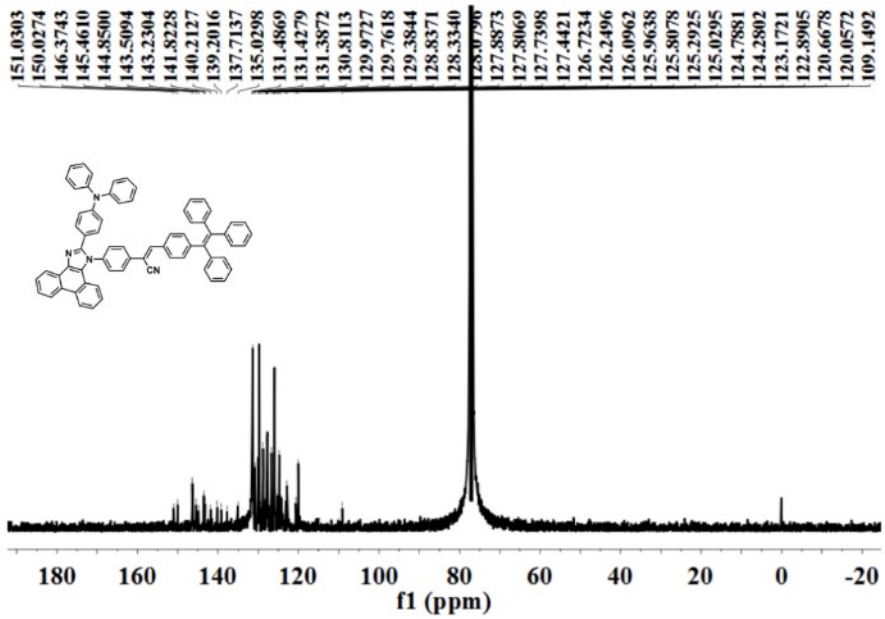


Fig. S14. ^{13}C NMR spectrum of compound **M3** in $CDCl_3$.

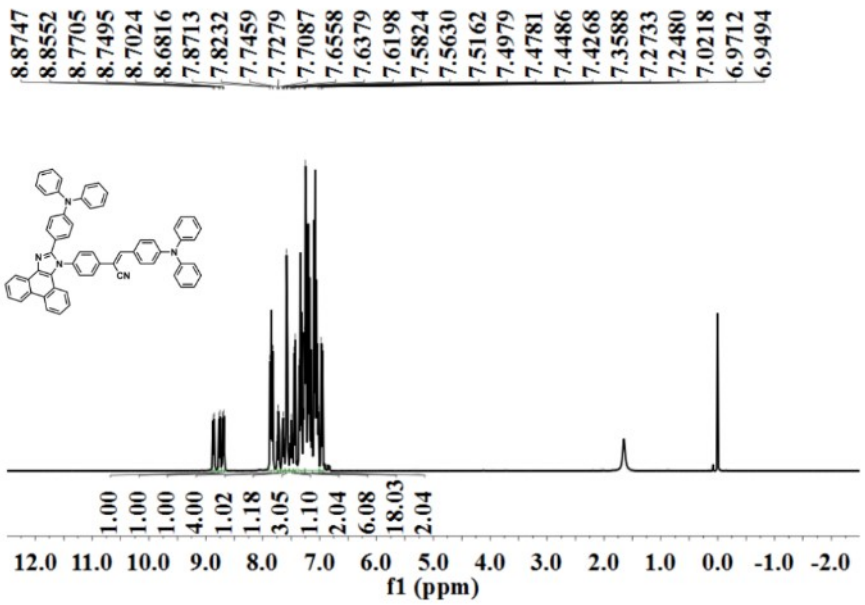


Fig. S15. ^{1}H NMR spectrum of compound **M4** in $CDCl_3$.

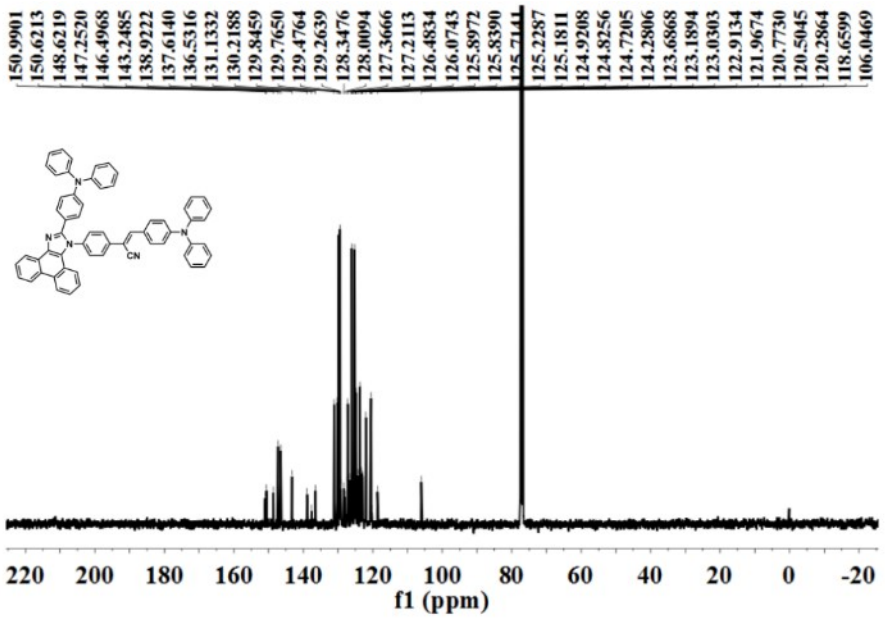


Fig. S16. ^{13}C NMR spectrum of compound **M4** in $CDCl_3$.