Electronic Supplementary Information

Crystal structures, dual-state emissions and polymer-based doped room-temperature phosphorescence of 8-benzyloxyisoquinoline derivatives

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Contents:

8-(Benzyloxy)-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-H). White solid (316.9 mg), 85.3% yield, m. p. 141.2-141.8 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 7.52 (d, J = 7.0 Hz, 2H), 7.40-7.33 (m, 3H), 7.20 (s, 1H), 6.82 (s, 1H), 5.04 (s, 2H), 3.62 (br, 2H), 3.06 (br, 2H), 2.56 (s, 3H), 2.50 (s, 3H), 1.60-1.43 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.0, 158.8, 152.8, 143.8, 140.4, 136.0, 128.9, 128.3, 122.5, 116.4, 111.1, 110.6, 104.8, 78.7, 52.4, 25.5, 24.6, 24.2, 20.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{26}N_3O$, 372.2070; found, 372.2074.

3,6-Dimethyl-8-((4-methylbenzyl)oxy)-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-Me). White solid (337.3 mg), 87.5% yield, m. p. 123.8-123.9 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 7.39 (d, J = 7.0 Hz, 2H), 7.18-7.17 (m, 3H), 6.81 (s, 1H), 5.00 (s, 2H), 3.60 (br, 2H), 3.09 (br, 2H), 2.55 (s, 3H), 2.50 (s, 3H), 2.36 (s, 3H), 1.61-1.26 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 161.1, 158.8, 152.8, 143.8, 140.4, 138.1, 133.0, 129.02, 128.99, 122.4, 116.5, 110.9, 110.6, 104.8, 78.6, 52.3, 25.6, 24.6, 24.2, 21.2, 20.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{25}H_{28}N_3O$, 386.2227; found, 386.2231.

Methyl 4-(((7-cyano-3,6-dimethyl-1-(piperidin-1-yl)isoquinolin-8-yl)oxy) methyl) benzoate (IQ-COOMe). White solid (348.8 mg), 81.2% yield, m. p. 146.8-147.5 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 8.06 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 7.0 Hz, 2H), 7.23 (s, 1H), 6.83 (s, 1H), 5.09 (s, 2H), 3.93 (s, 3H), 3.60 (br, 2H), 3.04 (br, 2H), 2.57 (s, 3H), 2.51 (s, 3H), 1.55 (br, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 166.8, 160.7, 158.8, 153.0, 143.8, 141.2, 140.4, 130.0, 129.7, 128.3, 122.7, 116.3, 111.2, 110.5, 104.7, 77.7, 52.4, 52.0, 25.6, 24.5, 24.2, 20.6 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{26}H_{27}N_3O_3Na$, 452.1945; found, 452.1943.

8-((4-Fluorobenzyl)oxy)-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-F). White solid (297.9 mg), 76.5% yield, m. p. 159.6-159.7 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 7.49-7.46 (m, 2H), 7.21 (s, 1H), 7.07-7.04 (m, 2H), 6.82 (s, 1H), 5.00 (s, 2H), 3.63 (br, 2H), 3.05 (br, 2H), 2.55 (s, 3H), 2.50 (s, 3H), 1.59 (br, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.8 (d, J = 246.3 Hz), 160.7, 158.8, 153.0, 143.8, 140.4, 131.9 (d, J = 3.8 Hz), 130.8 (d, J = 7.5 Hz), 122.6, 116.4, 115.2 (d, J = 21.3 Hz), 111.1, 110.6, 104.9, 77.8, 52.4, 25.6, 24.6, 24.2, 20.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{25}FN_3O$, 390.1976; found, 390.1976.

8-((4-Chlorobenzyl)oxy)-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-Cl). White solid (318.2 mg), 78.4% yield, m. p. 142.8-143.5 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 7.45 (d, J = 7.5 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.21 (s, 1H), 6.83 (s, 1H), 5.00 (s, 2H), 3.62 (br, 2H), 3.02 (br, 2H), 2.56 (s, 3H), 2.50 (s, 3H), 1.58 (br, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.7, 158.8, 152.9, 143.7, 140.4, 134.6, 134.2, 130.1, 128.5, 122.7, 116.4, 111.1, 110.5, 104.8, 77.6, 52.4, 25.6, 24.5, 24.2, 20.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{25}ClN_3O$, 406.1681; found, 406.1683.

8-((4-Bromobenzyl)oxy)-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-Br). White solid (340.0 mg), 75.5% yield, m. p. 163.0-163.6 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 7.51 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.21 (s, 1H), 6.83 (s, 1H), 4.99 (s, 2H), 3.60 (br, 2H), 3.01 (br, 2H), 2.56 (s, 3H), 2.50 (s, 3H), 1.58 (br, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 160.7,

158.8, 153.0, 143.8, 140.4, 135.1, 131.5, 130.4, 122.7, 122.4, 116.4, 111.1, 110.5, 104.8, 77.7, 52.4, 25.6, 24.6, 24.2, 20.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{25}BrN_3O$, 450.1176; found, 450.1170.

8-((4-Cyanobenzyl)oxy)-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-CN). White solid (293.0 mg), 73.9% yield, m. p. 174.3-175.2 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 7.71-7.66 (m, 4H), 7.25 (s, 1H), 6.86 (s, 1H), 5.09 (s, 2H), 3.62 (br, 2H), 3.00 (br, 2H), 2.57 (s, 3H), 2.51 (s, 3H), 1.65-1.56 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.4, 158.8, 153.2, 143.8, 141.5, 140.5, 132.3, 128.8, 123.0, 118.6, 116.3, 112.1, 111.4, 110.5, 104.7, 77.1, 52.5, 25.7, 24.5, 24.2, 20.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{25}H_{24}N_4O$, 397.2023; found, 397.2014.

3,6-Dimethyl-8-((4-nitrobenzyl)oxy)-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-NO_2). Yellow solid (324.8 mg), 78.0% yield, m. p. 208.5-209.4 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 8.27 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 9.0 Hz, 2H), 7.26 (s, 1H), 6.87 (s, 1H), 5.15 (s, 2H), 3.62 (br, 2H), 3.01 (br, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 1.55 (br, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 160.3, 158.8, 153.2, 147.8, 143.8, 143.5, 140.5, 128.8, 123.7, 123.1, 116.2, 111.4, 110.5, 104.7, 76.8, 52.5, 25.7, 24.5, 24.2, 20.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{24}H_{25}N_4O_3$, 417.1921; found, 417.1928.

8-((3,5-Dimethylbenzyl)oxy)-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-DMe). White solid (364.4 mg), 91.2% yield, m. p. 122.1-123.0 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 7.19 (s, 1H), 7.12 (s, 2H), 6.97 (s, 1H), 6.80 (s, 1H), 4.96 (s, 2H), 3.60 (br, 2H), 3.09 (br, 2H), 2.56 (s, 3H), 2.49 (s, 3H), 2.32 (s, 6H), 1.61-1.48 (m, 6H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 161.2, 158.8, 152.8, 143.8, 140.4, 137.8, 135.8, 129.9, 126.9, 122.3, 116.5, 110.8, 110.6, 104.8, 78.9, 52.3, 25.5, 24.7, 24.2, 21.2, 20.6 ppm. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{26}H_{30}N_3O$, 400.2383; found, 400.2384.

8-((3,5-Bis(trifluoromethyl)benzyl)oxy)-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (IQ-BTF). White solid (348.6 mg), 68.7% yield, m. p. 104.9-105.7 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): 8.00 (s, 2H), 7.88 (s, 1H), 7.26 (s, 1H), 6.86 (s, 1H), 5.15 (s, 2H), 3.60 (br, 2H), 3.00 (br, 2H), 2.58 (s, 3H), 2.52 (s, 3H), 1.58 (br, 6H) ppm.^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.0, 158.8, 153.2, 143.8, 140.5, 138.6, 132.1 (q, J = 33.8 Hz), 128.7 (d, J = 3.75 Hz), 125.4 (q, J = 270.0 Hz), 124.3, 123.2, 122.3-122.2 (m), 122.1, 116.2, 111.4, 110.5, 104.9, 76.6, 52.5, 25.7, 24.4, 24.2, 20.6. HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{26}H_{24}F_6N_3O$, 508.1818; found, 508.1816.

1.3 Preparation of the doped materials

Dissolve the specific amount of isoquinoline derivative and PMMA in dichloromethane, respectively. The solutions were treated with ultrasound for 10 min in the ultrasonic instrument. The mixture was prepared by drop-wise addition of isoquinoline solution into PMMA solution, and then was treated with ultrasound for 10 min in the ultrasonic instrument for uniform

dissolution. Then the fully mixed two-component solution was slowly poured into the mold. Finally, thin and transparent film was obtained after drying the mixture at 50 °C for 2 h.

2. Figures and tables

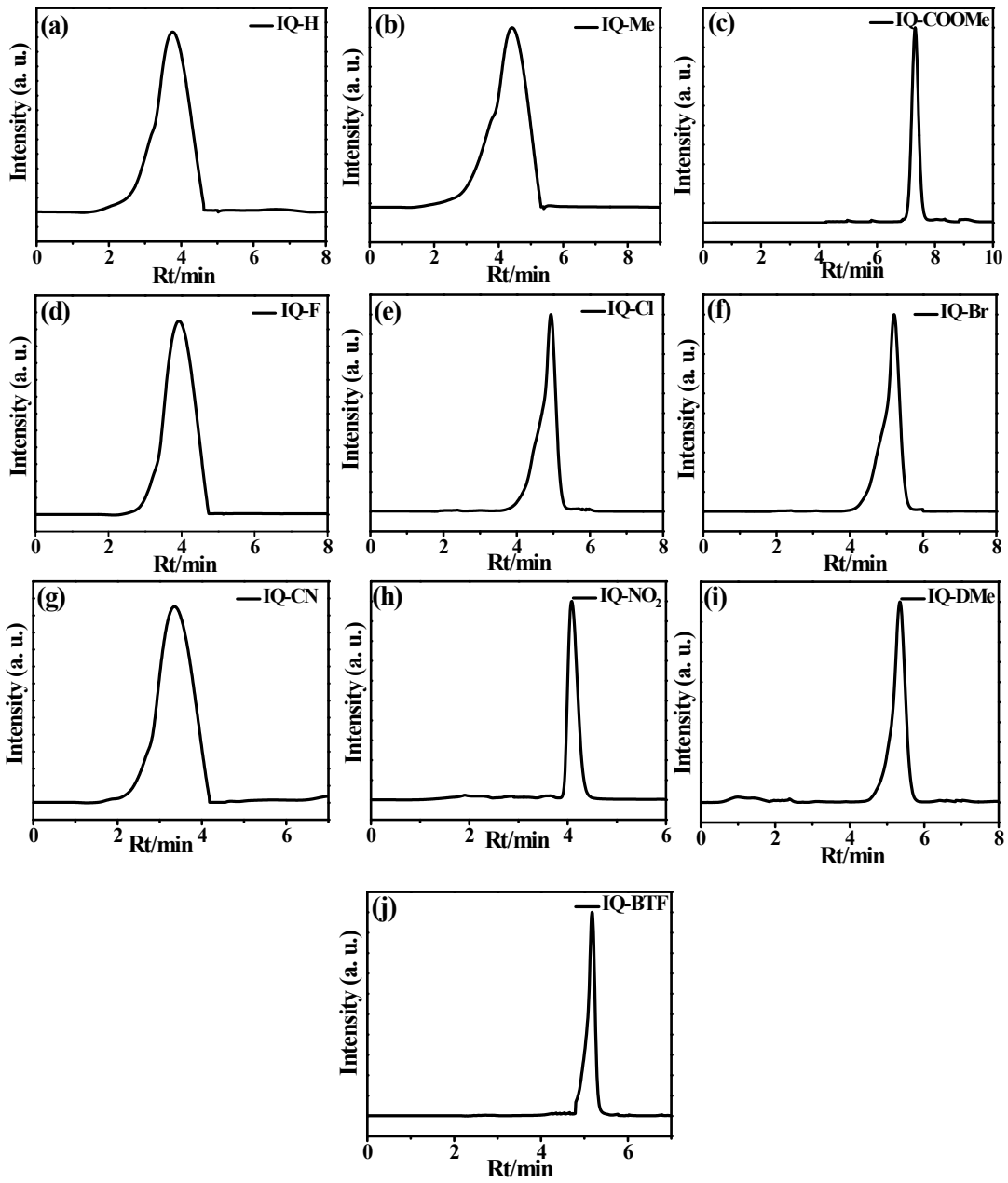

Fig. S1 High performance liquid chromatography of 8-benzyloxyisoquinoline derivatives. Conditions: CH_3CN/H_2O = 60%:40% for (a); CH_3CN/H_2O = 80%:20% for (b); CH_3OH/H_2O = 60%:40% for (c)-(j).

Table S1 Fluorescence properties of 8-benzyloxyisoquinoline derivatives

compound	λ_{abs}^{max} THF, nm	λ_{em}^{max} THF, nm	λ_{abs}^{max} Solid, nm	λ_{em}^{max} Solid, nm	$\Phi_{Fluo.}$ Solid, %
IQ-H	352	441	417	455	58.3
IQ-Me	353	446	401	443	62.1
IQ-COOMe	351	407	373	455	9.6
IQ-F	353	445	411	449	57.5
IQ-Cl	353	436	400	456	34.2
IQ-Br	354	437	422	466	35.3
IQ-CN	351	407	397	465	7.6
IQ-NO_2	349	406	403	495	0.9
IQ-DMe	353	436	432	461	48.1
IQ-BTF	351	406	402	458	13.6

Table S2 Crystal data and details of collection and refinement for **IQ-H**, **IQ-Me**, **IQ-COOMe**, **IQ-F**, and **IQ-Cl**

	IQ-H	**IQ-Me**	**IQ-COOMe**	**IQ-F**	**IQ-Cl**
CCDC (no.)	2245980	2245981	2245985	2245982	2245983
Empirical formula	$C_{24}H_{25}N_3O$	$C_{25}H_{27}N_3O$	$C_{26}H_{27}N_3O_3$	$C_{24}H_{24}FN_3O$	$C_{24}H_{24}ClN_3O$
Formula weight	371.47	385.49	429.50	389.46	405.91
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space group	$P\,2_1$	P ccn	$P\bar{1}$	P bca	$P\,2_1$
Z	2	8	4	8	4
D_{calcd} [Mg/m^3]	1.197	1.071	1.251	1.270	1.240
F (000)	396	1648	912	1648	856
θ range [°]	2.480-25.997	2.538-25.496	1.854-26.000	2.553-24.993	2.411-25.499
R_1 [I>2σ(I)]	0.0346	0.0641	0.0479	0.0749	0.0486
wR_2 [I>2σ(I)]	0.0796	0.1607	0.1174	0.1566	0.1063
a [Å]	6.8819(4)	15.3952(10)	11.0228(14)	19.673(7)	10.7226(8)
b [Å]	18.2382(10)	31.5081(17)	11.0661(13)	7.589(2)	13.7126(11)
c [Å]	8.3735(5)	9.8531(6)	19.024(3)	27.281(7)	14.8083(13)
α [deg]	90	90	80.438(4)	90	90
β [deg]	101.220(2)	90	87.096(4)	90	93.229(3)
γ [deg]	90	90	85.625(4)	90	90
V [Å^3]	1030.90(10)	4779.5(5)	2279.9(5)	4073(2)	2173.9(3)
GOF	1.048	1.030	1.050	1.034	1.033
R(int)	0.0272	0.0535	0.0369	0.1441	0.0273
No. of reflcns collected	10712	21207	33903	16722	17855
No. of unique reflcns	3649	4433	8916	3565	7991
R_1 (all data)	0.0401	0.1147	0.0693	0.1827	0.0829

wR_2 (all data)	0.0839	0.1887	0.1338	0.2194	0.1262

Table S3 Crystal data and details of collection and refinement for **IQ-Br**, **IQ-CN**, **IQ-NO$_2$**, **IQ-DMe**, and **IQ-BTF**

	IQ-Br	**IQ-CN**	**IQ-NO$_2$**	**IQ-DMe**	**IQ-BTF**
CCDC (no.)	2245984	2245986	2245987	2245988	2245989
Empirical formula	$C_{24}H_{24}BrN_3O$	$C_{25}H_{24}N_4O$	$C_{24}H_{24}N_4O_3$	$C_{26}H_{29}N_3O$	$C_{26}H_{23}F_6N_3O$
Formula weight	450.37	396.48	416.47	399.52	507.47
Temperature (K)	293(2)	296(2)	296(2)	293(2)	296(2)
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*C* 2/c	*P*$\bar{1}$	*P* 2_1	*P*$\bar{1}$	*P*$\bar{1}$
Z	8	2	4	2	4
D_{calcd} [Mg/m^3]	1.391	1.250	1.276	1.176	1.344
F (000)	1856	420	880	428	1048
θ range [°]	2.336-25.500	2.897-25.499	2.349-25.500	1.881-25.498	2.449-25.500
R_1 [I>2σ(I)]	0.0503	0.0577	0.0487	0.0566	0.0499
wR_2 [I>2σ(I)]	0.1295	0.1540	0.1011	0.1564	0.1192
a [Å]	21.3712(7)	7.8031(3)	10.7300(9)	10.8627(3)	9.4961(3)
b [Å]	10.6818(3)	10.8097(4)	13.6341(10)	10.9176(3)	16.3124(5)
c [Å]	19.0014(6)	13.6803(5)	14.8150(14)	10.9887(4)	17.0312(6)
α [deg]	90	104.0820(10)	90	80.5480(10)	75.8520(10)
β [deg]	97.4240(10)	92.9470(10)	90.254(3)	87.9690(10)	84.4340(10)
γ [deg]	90	108.1090(10)	90	61.5120(10)	78.9830(10)
V [Å^3]	4301.3(2)	1053.66(7)	2167.3(3)	1128.47(6)	2507.53(14)
GOF	1.042	1.061	1.071	1.048	1.032
R(int)	0.0365	0.0710	0.0199	0.0246	0.0513
No. of reflcns collected	20532	14730	10438	11024	36842
No. of unique reflcns	3993	3919	7518	4161	9300
R_1 (all data)	0.0826	0.0743	0.0792	0.0733	0.0811
wR_2 (all data)	0.1504	0.1689	0.1224	0.1747	0.1418

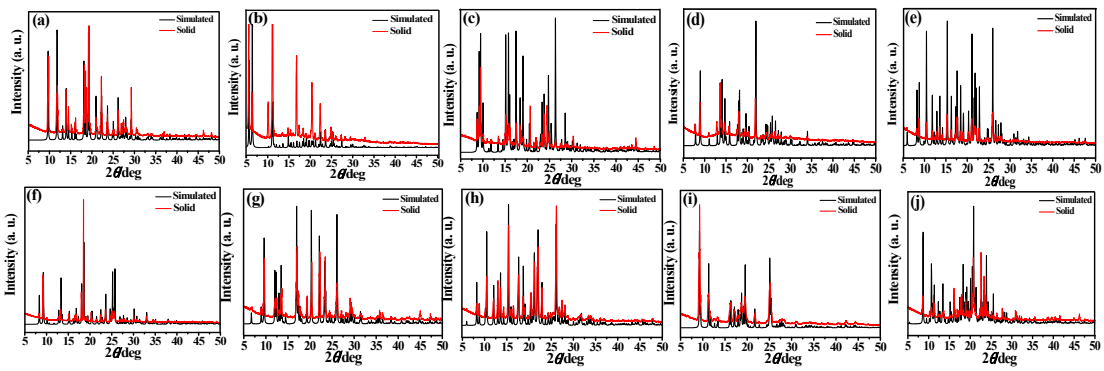

Fig. S2 Comparison of experimental XRD curves and the simulated XRD curves obtained from the corresponding single crystals: (a) **IQ-H**; (b) **IQ-Me**; (c) **IQ-COOMe**; (d) **IQ-F**; (e) **IQ-Cl**; (f) **IQ-Br**; (g) **IQ-CN**; (h) **IQ-NO$_2$**; (i) **IQ-DMe**; (j) **IQ-BTF**.

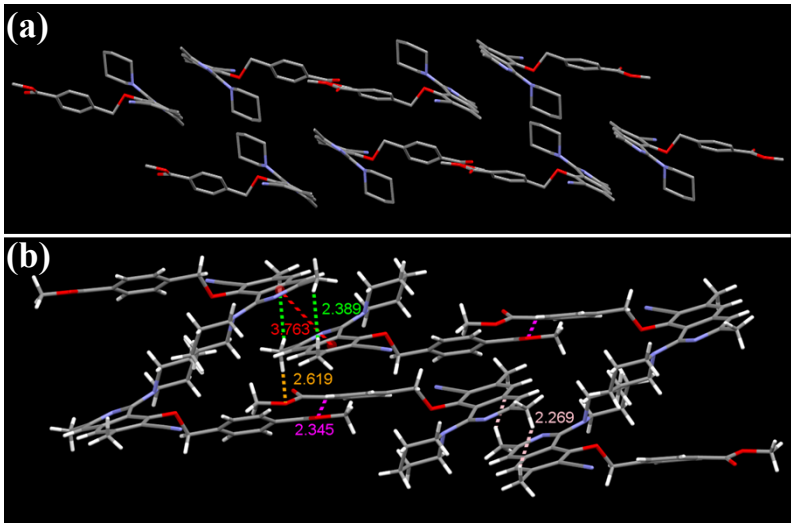

Fig. S3 Stacking arrangement (a) and intermolecular interactions (b) in crystal **IQ-COOMe**.

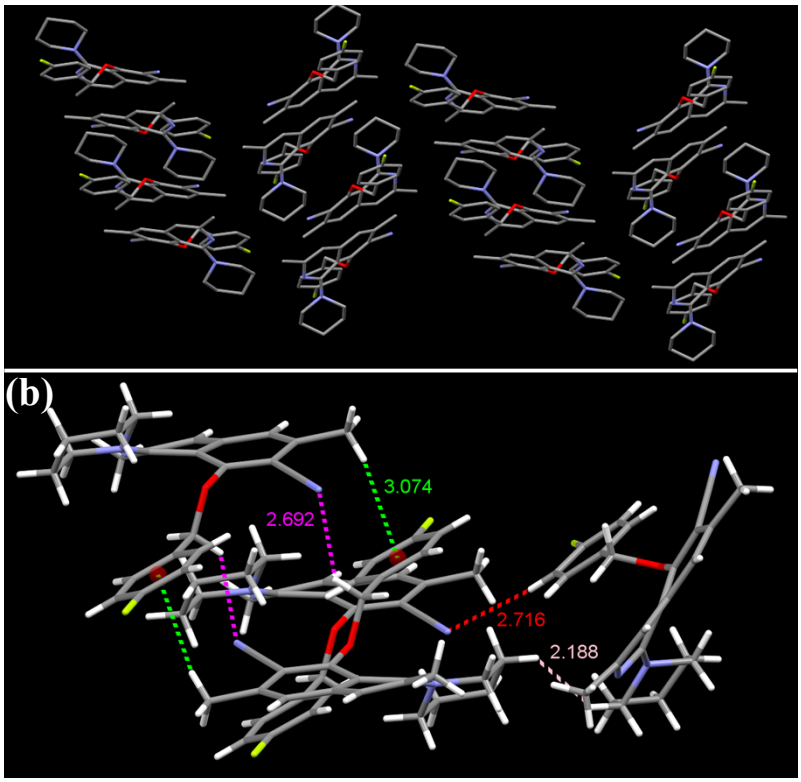

Fig. S4 Stacking arrangement (a) and intermolecular interactions (b) in crystal **IQ-F**.

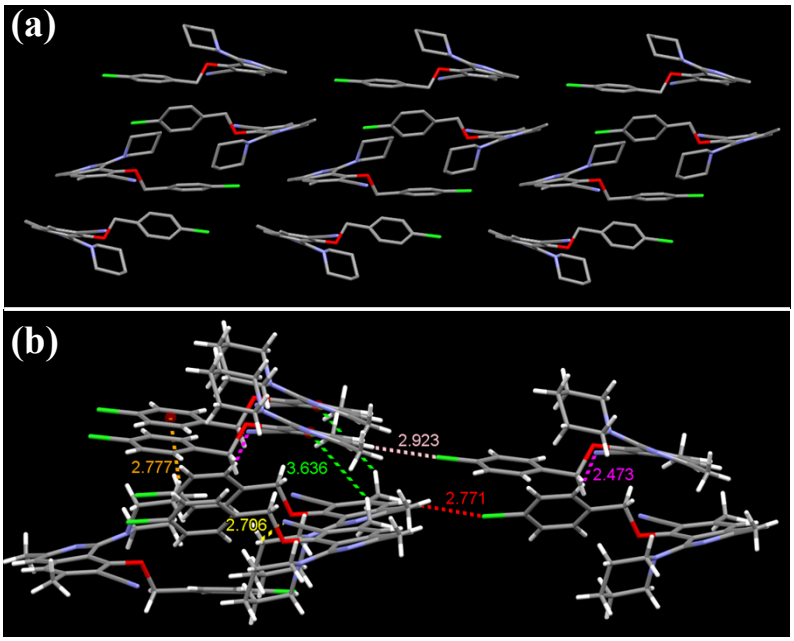

Fig. S5 Stacking arrangement (a) and intermolecular interactions (b) in crystal **IQ-Cl**.

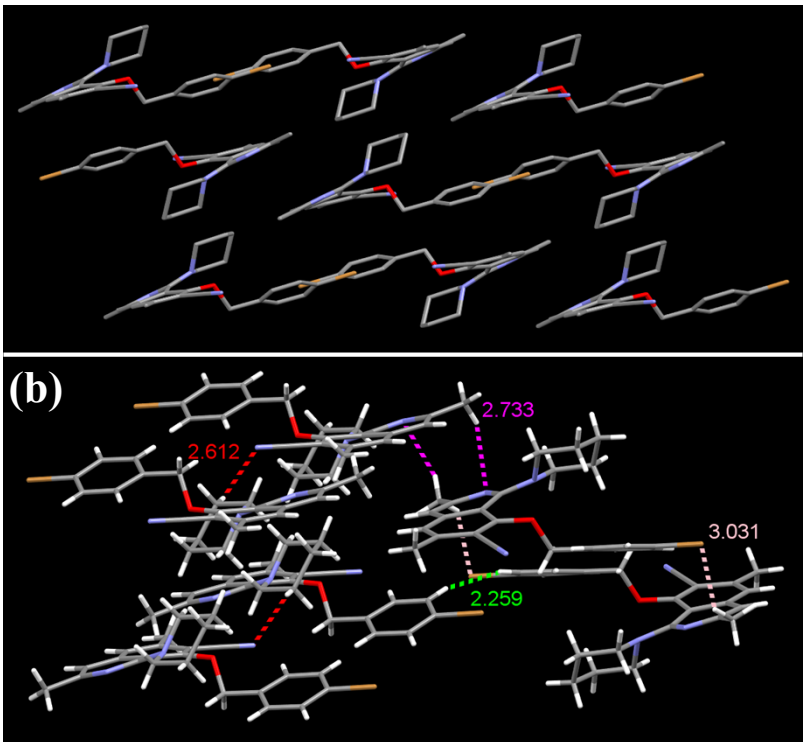

Fig. S6 Stacking arrangement (a) and intermolecular interactions (b) in crystal **IQ-Br**.

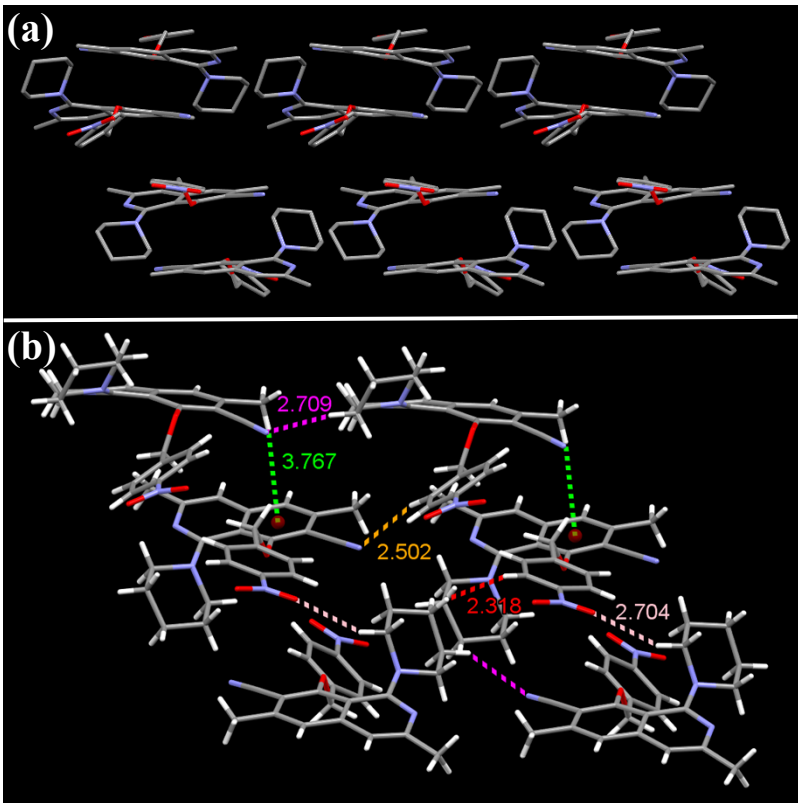

Fig. S7 Stacking arrangement (a) and intermolecular interactions (b) in crystal **IQ-NO_2**.

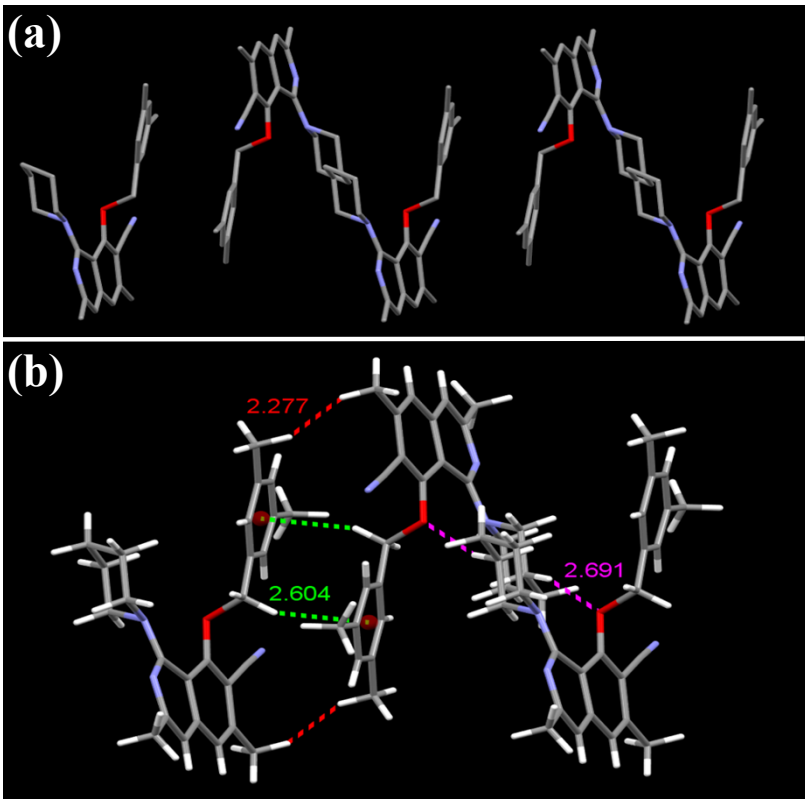

Fig. S8 Stacking arrangement (a) and intermolecular interactions (b) in crystal **IQ-DMe**.

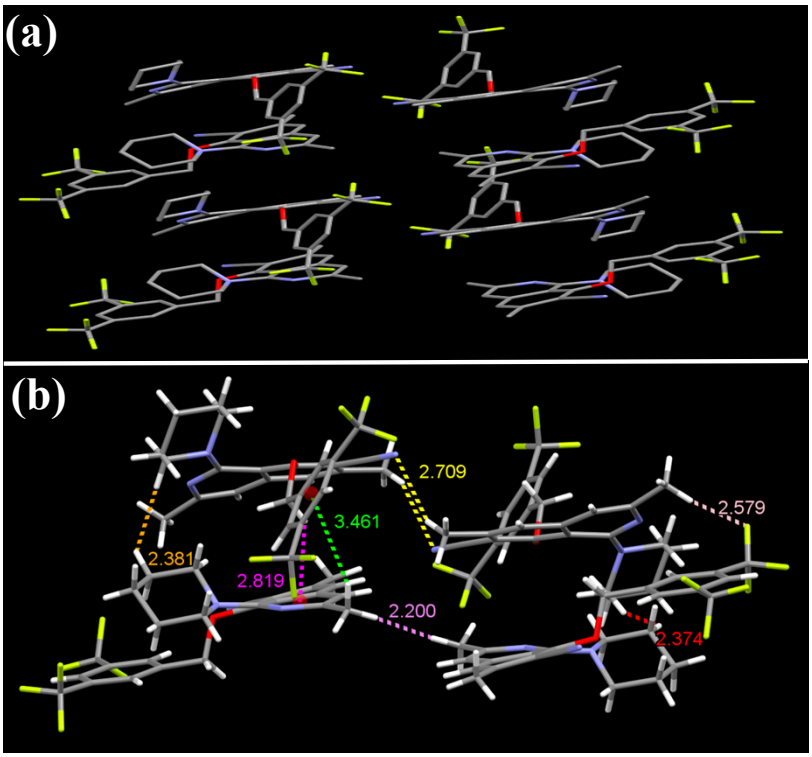

Fig. S9 Stacking arrangement (a) and intermolecular interactions (b) in crystal **IQ-BTF**.

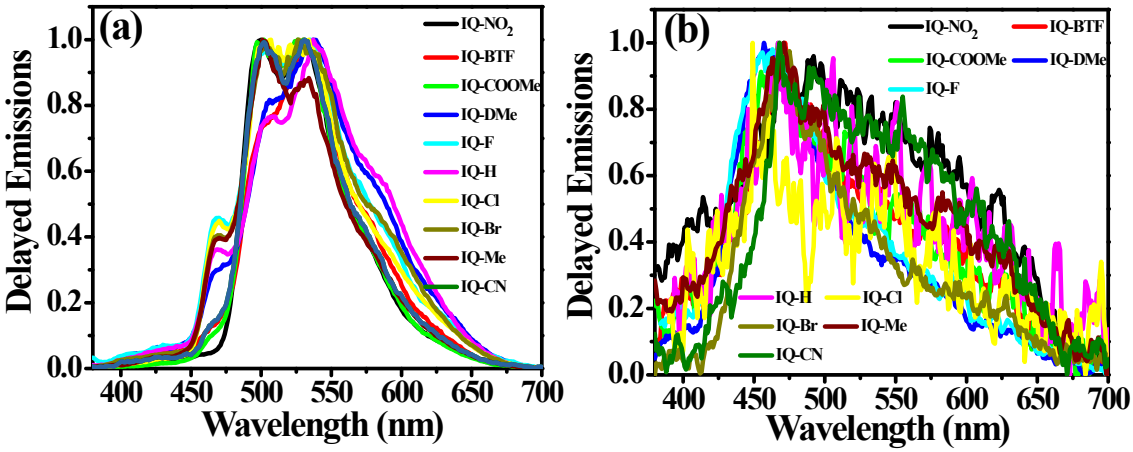

Fig. S10 (a) Delayed emission spectra of 8-benzyloxyisoquinoline derivatives in THF solvent (1×10^{-5} mol/L) at 77 K (λ_{ex}: 400 nm). (b) Delayed emission spectra of 8-benzyloxyisoquinoline derivatives in solid state at room temperature. Delay time: 0.5 ms.

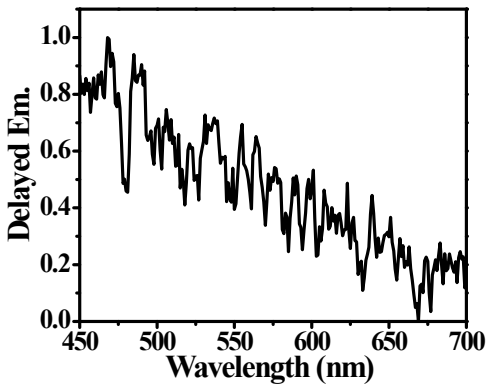

Fig. S11 Delayed spectrum of the PMMA polymer in solid state at room temperature (Delay time: 0.5 ms).

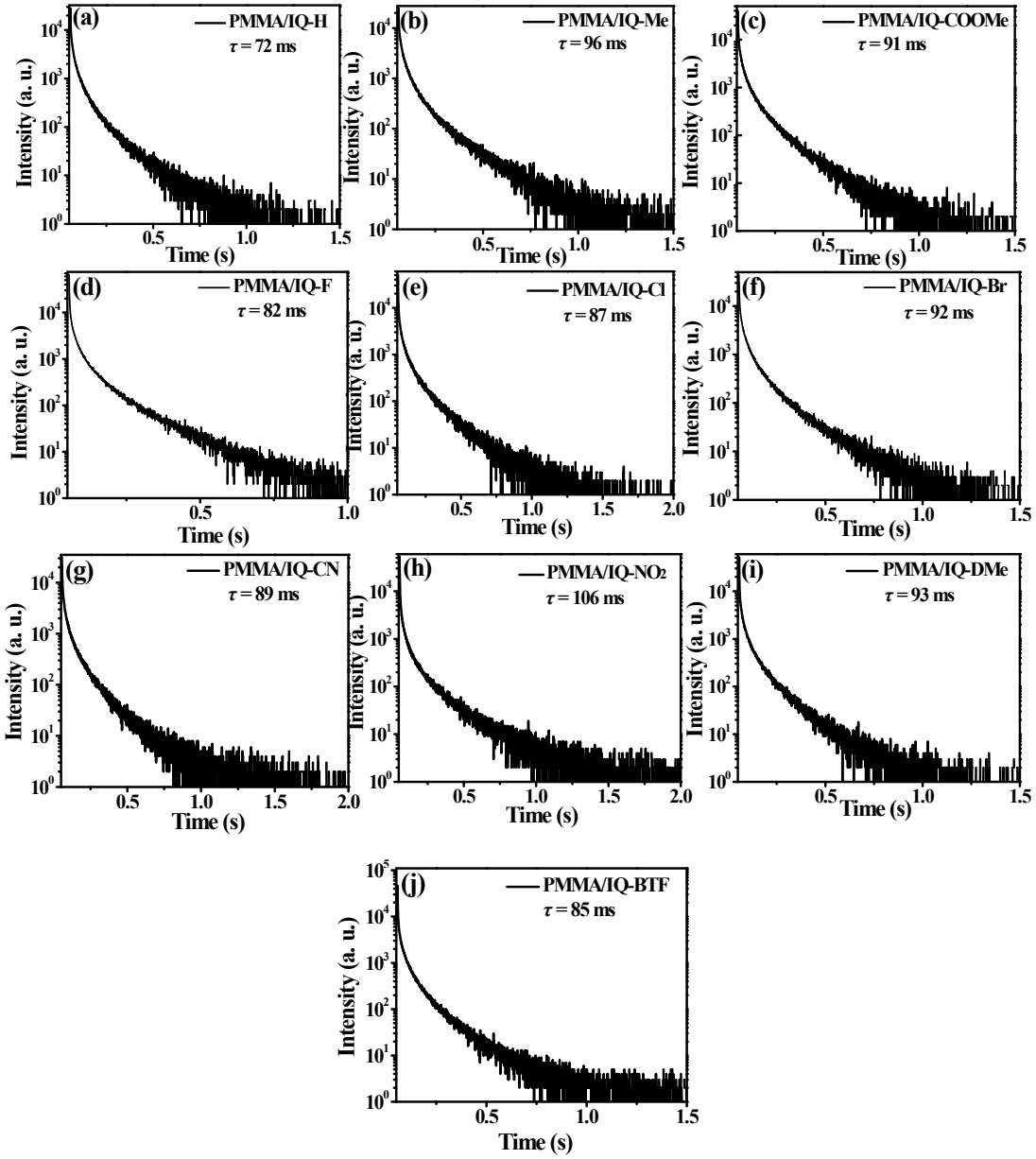

Fig. S12 Delayed emission lifetimes of the polymer-based doped materials.

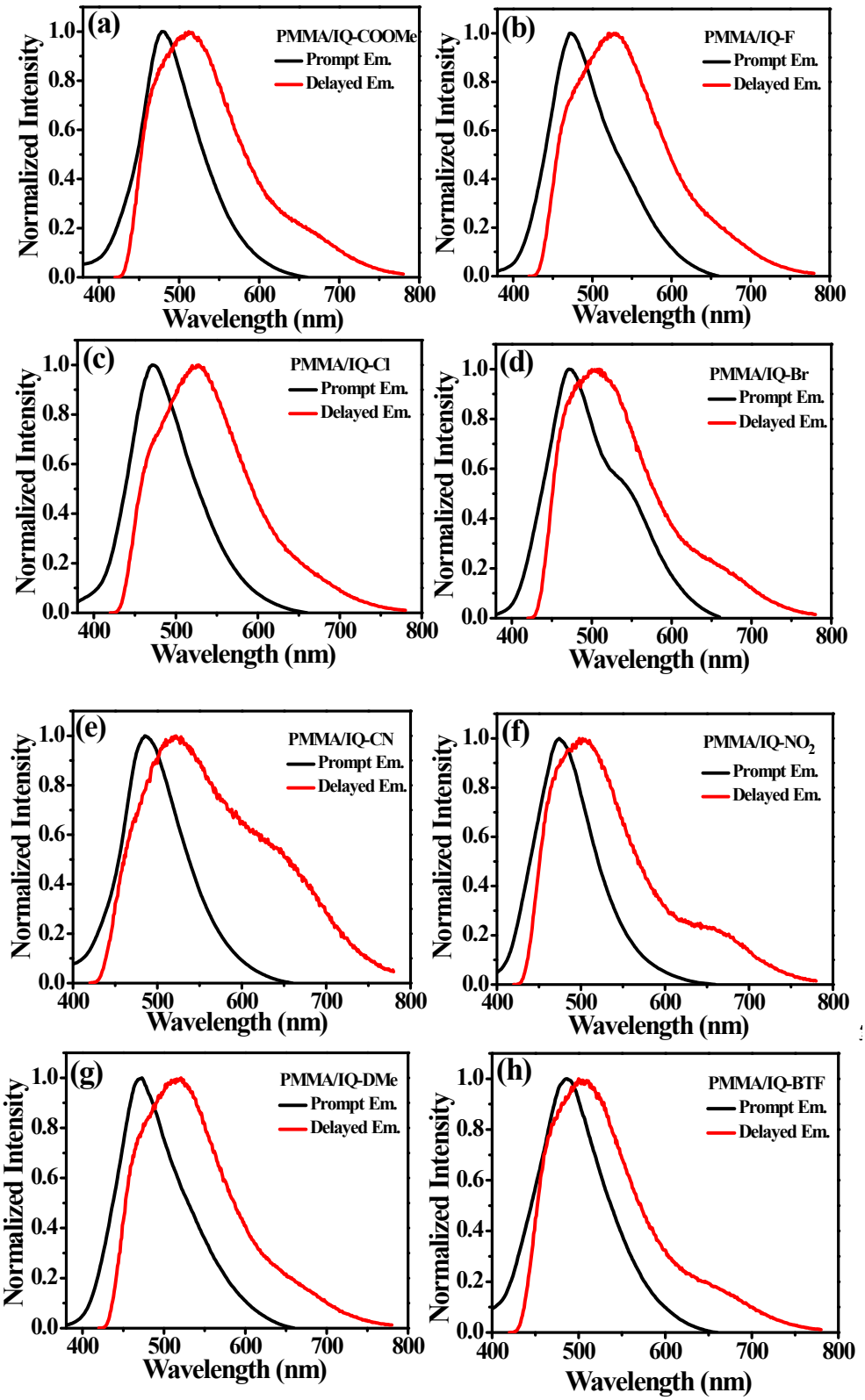

Fig. S13 Prompt and delayed spectra of the other two-component doped materials (λ_{ex} = 340 nm for prompt spectra and λ_{ex} = 400 nm for delayed spectra). Delay time: 0.5 ms.

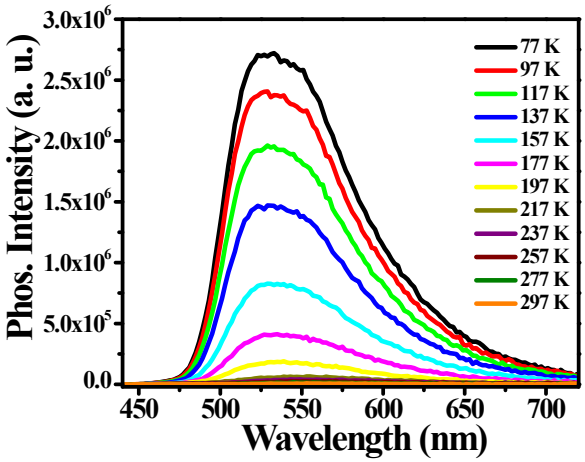

Fig. S14 Temperature-dependent delayed emissions of **PMMA/IQ-DMe** (λ_{ex} = 400 nm). Delay time: 0.5 ms.

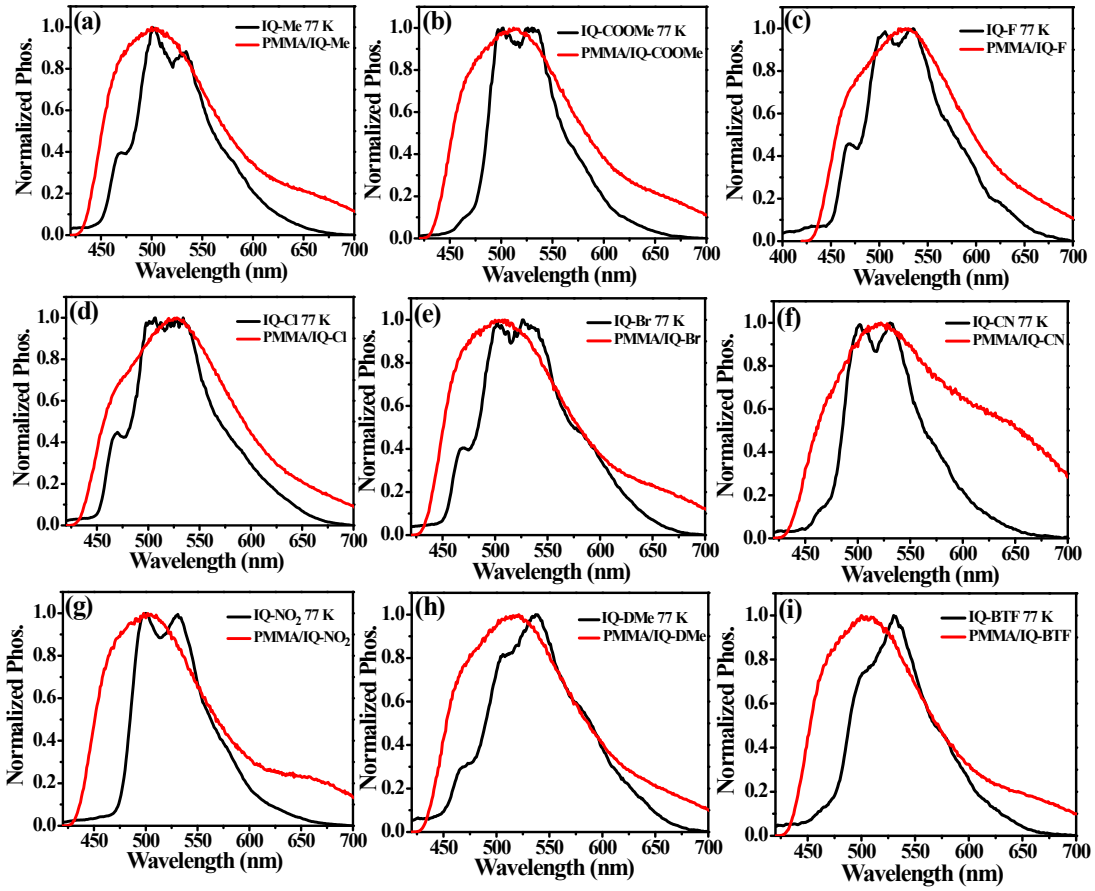

Fig. S15 Comparison of phosphorescence spectra between 8-benzyloxyisoquinoline derivatives at 77 K in THF solution (1×10^{-5} mol/L) and the corresponding two-component doped materials (λ_{ex} = 400 nm). Delay time: 0.5 ms.

3. Spectra of NMR

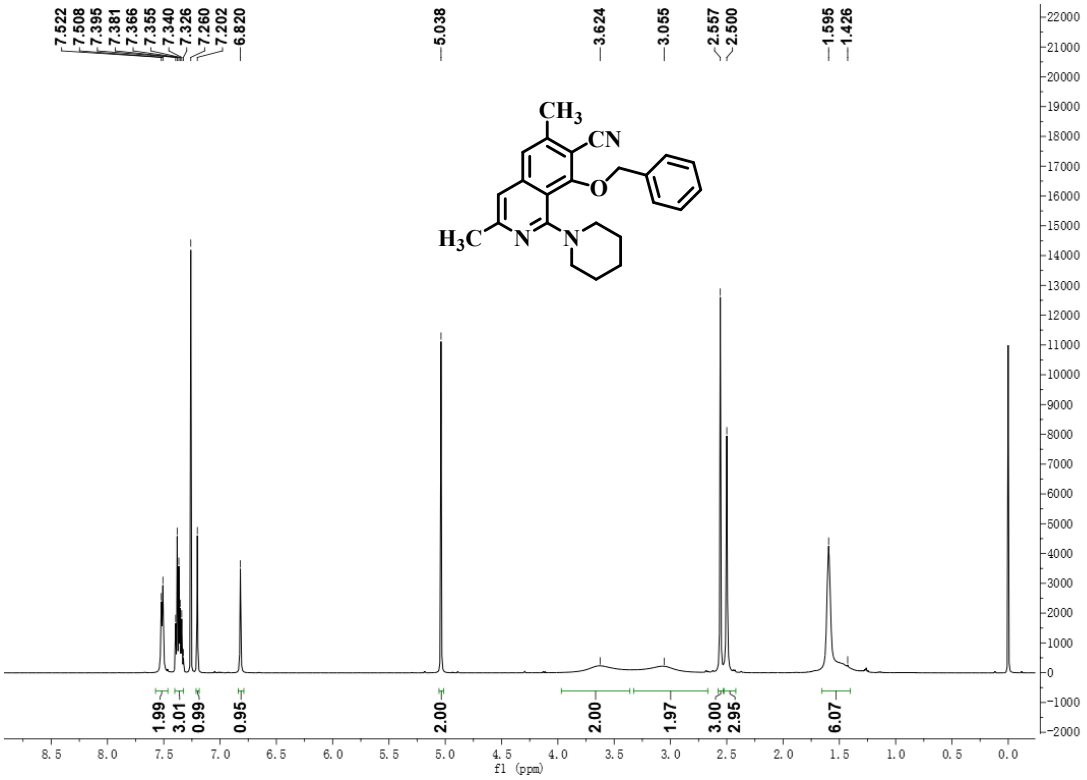

Fig. S16 ^{1}H NMR of **IQ-H** ($CDCl_3$, 500 MHz).

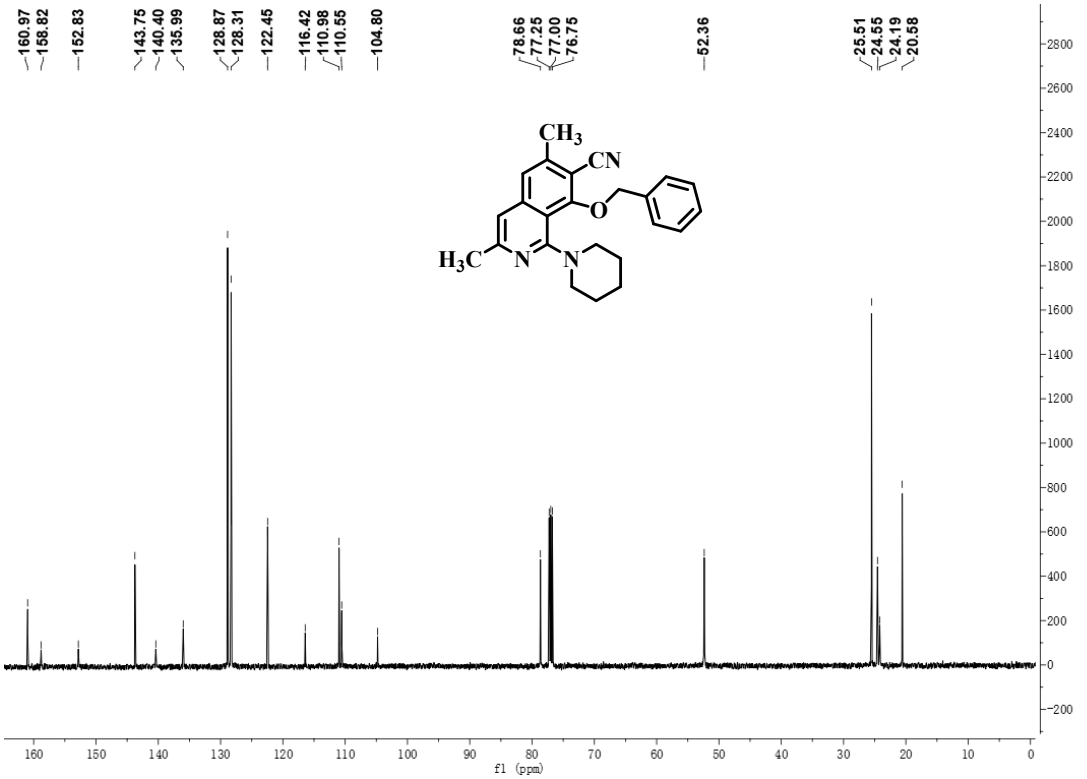

Fig. S17 ^{13}C NMR of **IQ-H** ($CDCl_3$, 125 MHz).

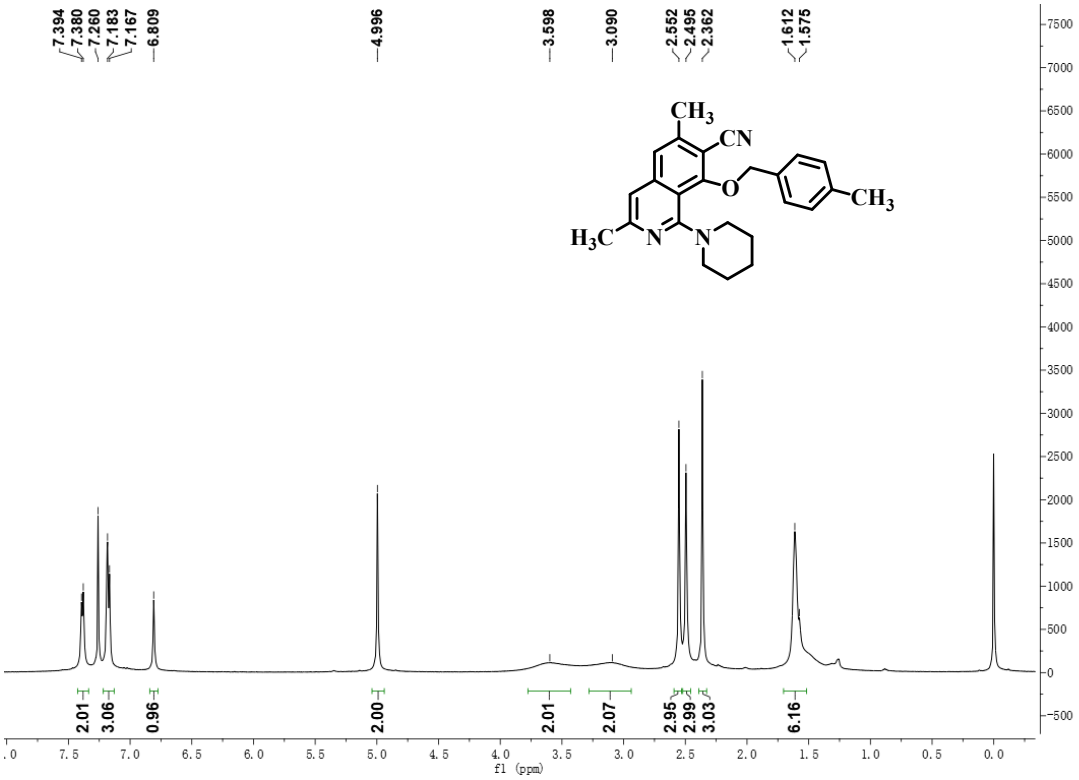

Fig. S18 ^{1}H NMR of **IQ-Me** ($CDCl_3$, 500 MHz).

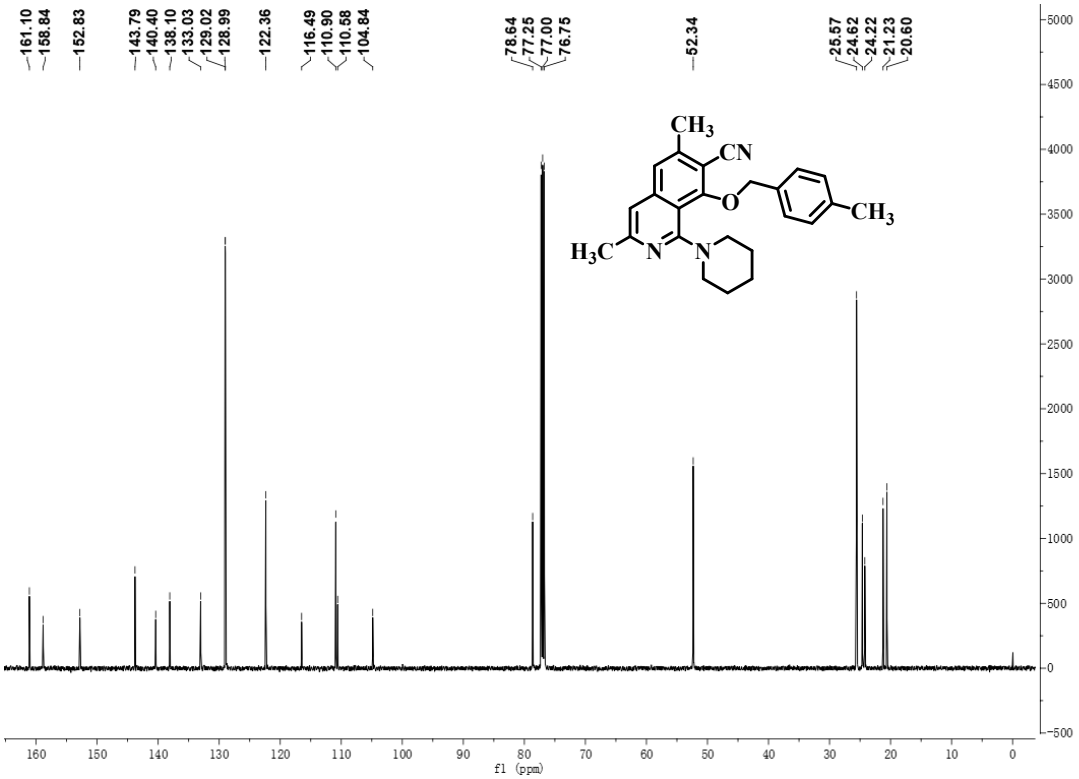

Fig. S19 ^{13}C NMR of **IQ-Me** ($CDCl_3$, 125 MHz).

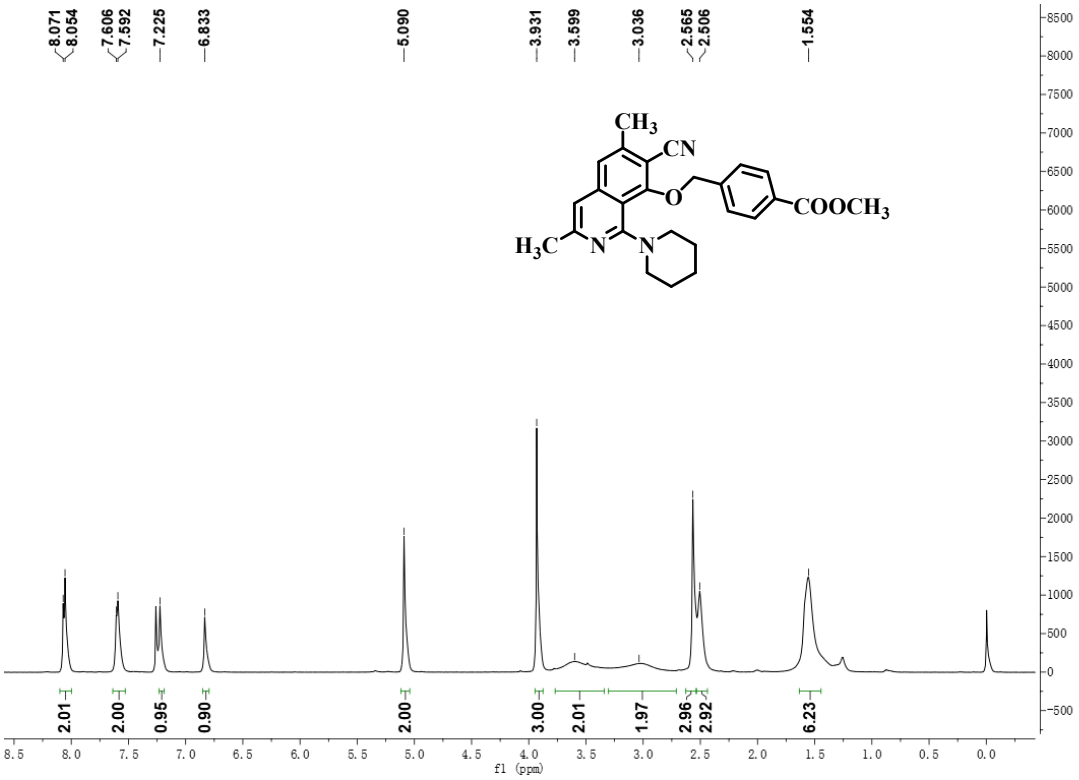

Fig. S20 ^{1}H NMR of **IQ-COOMe** ($CDCl_3$, 500 MHz).

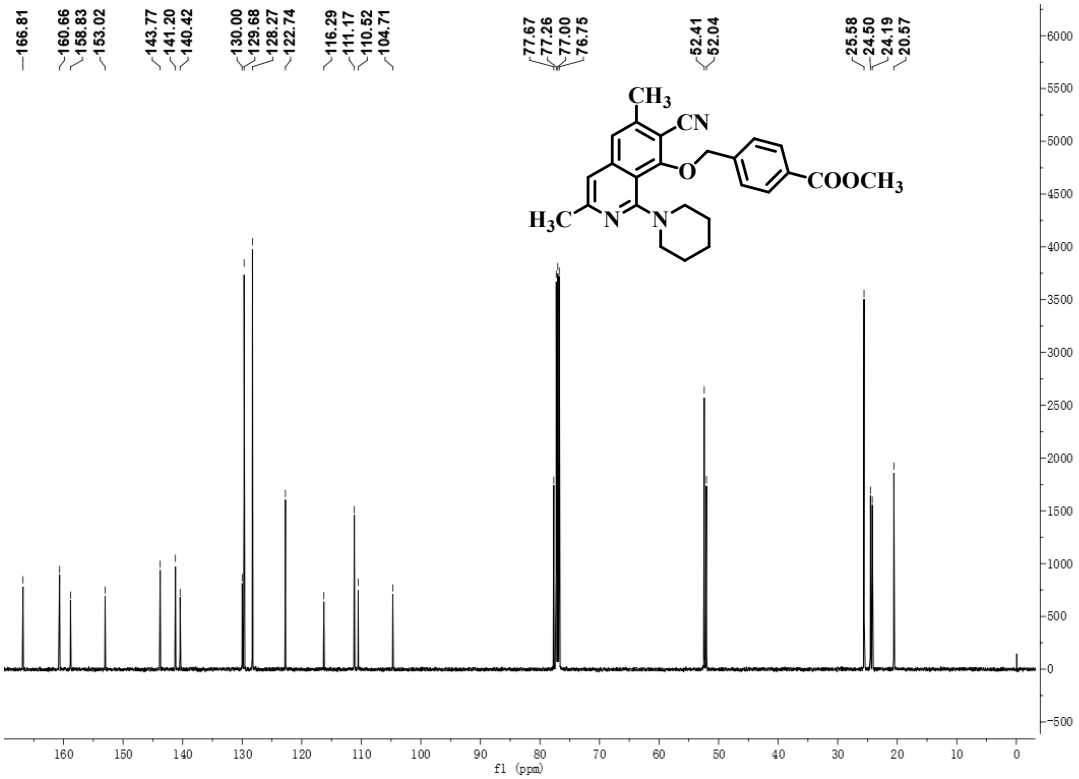

Fig. S21 ^{13}C NMR of **IQ-COOMe** ($CDCl_3$, 125 MHz).

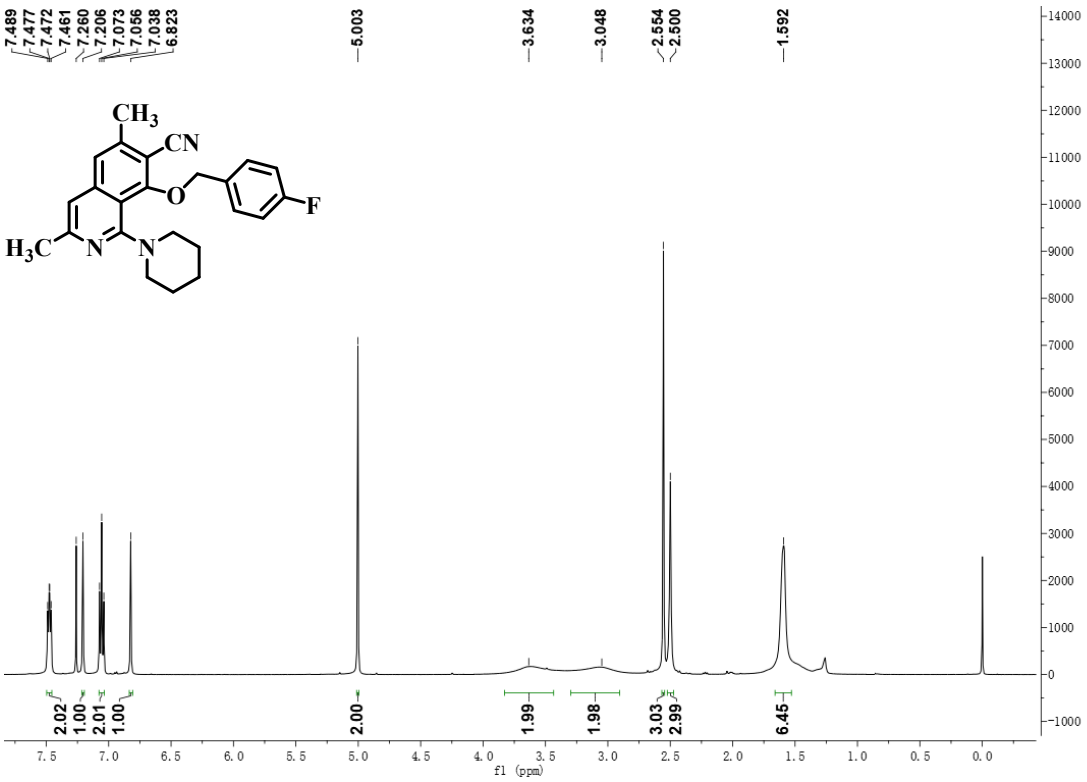

Fig. S22 ^{1}H NMR of **IQ-F** ($CDCl_3$, 500 MHz).

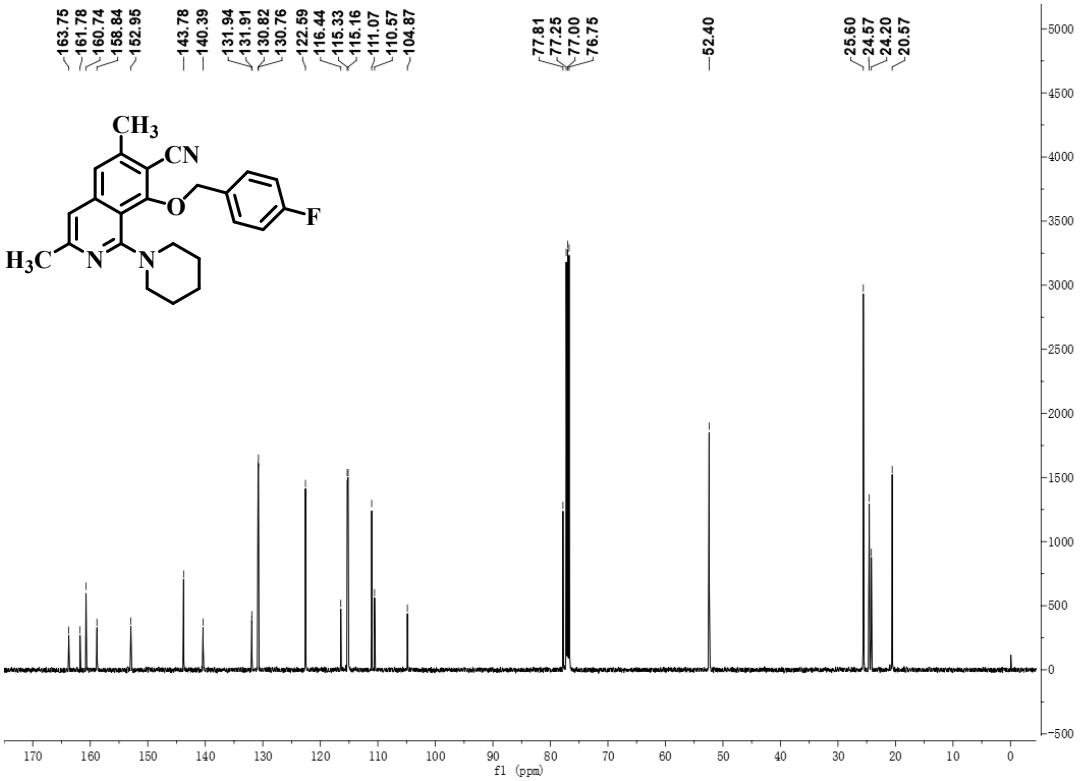

Fig. S23 ^{13}C NMR of **IQ-F** ($CDCl_3$, 125 MHz).

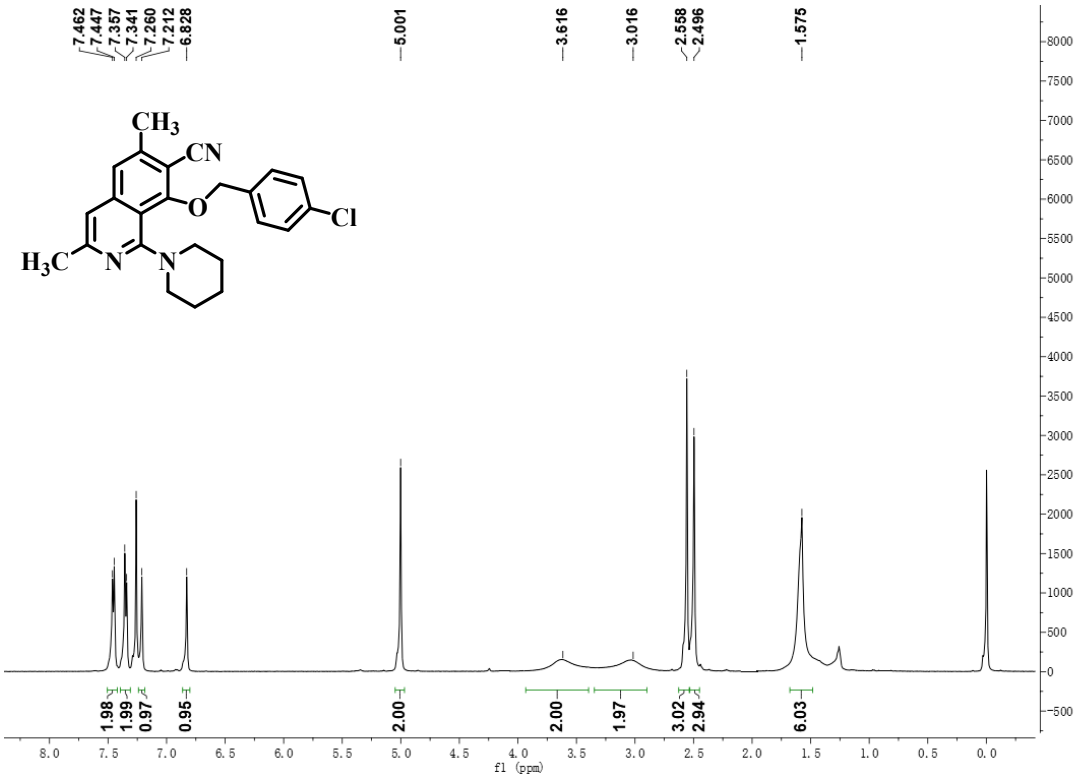

Fig. S24 ^{1}H NMR of **IQ-Cl** ($CDCl_3$, 500 MHz).

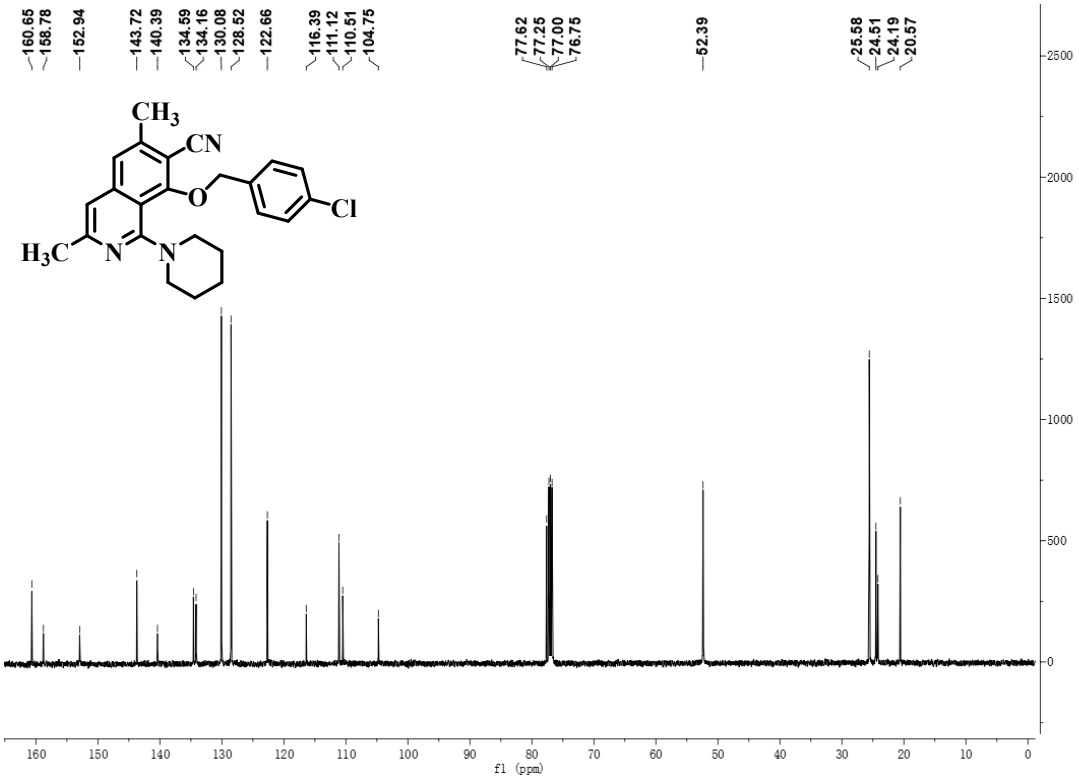

Fig. S25 ^{13}C NMR of **IQ-Cl** ($CDCl_3$, 125 MHz).

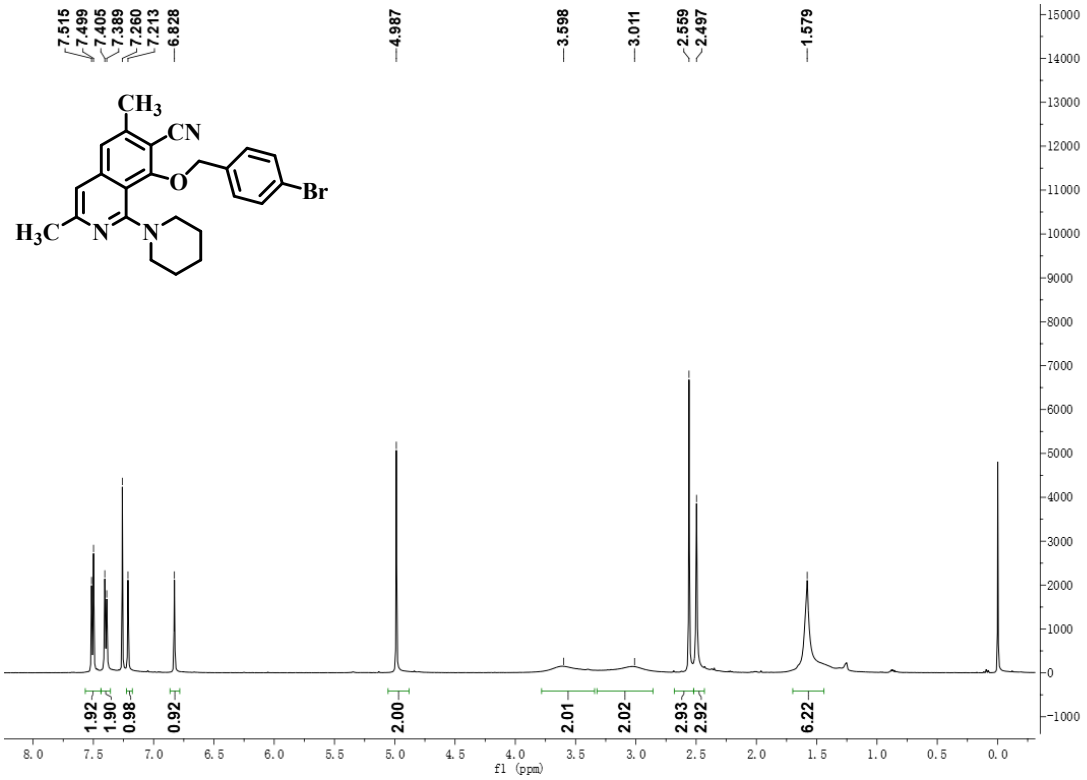

Fig. S26 ^{1}H NMR of **IQ-Br** ($CDCl_3$, 500 MHz).

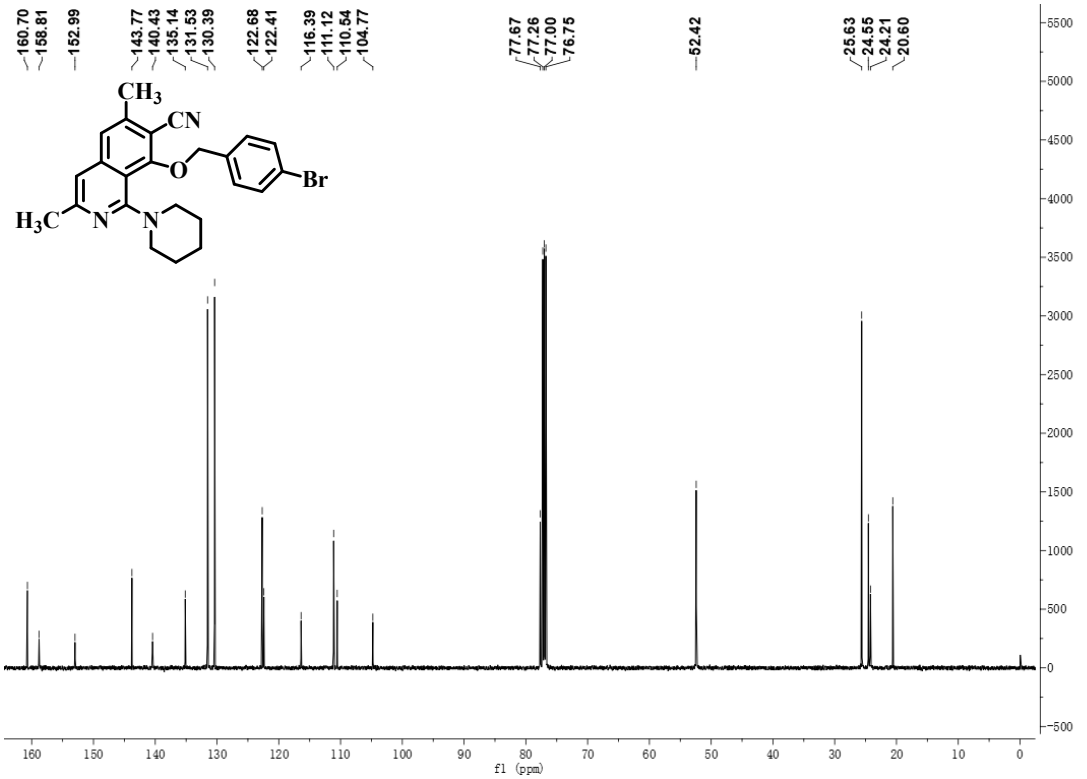

Fig. S27 ^{13}C NMR of **IQ-Br** ($CDCl_3$, 125 MHz).

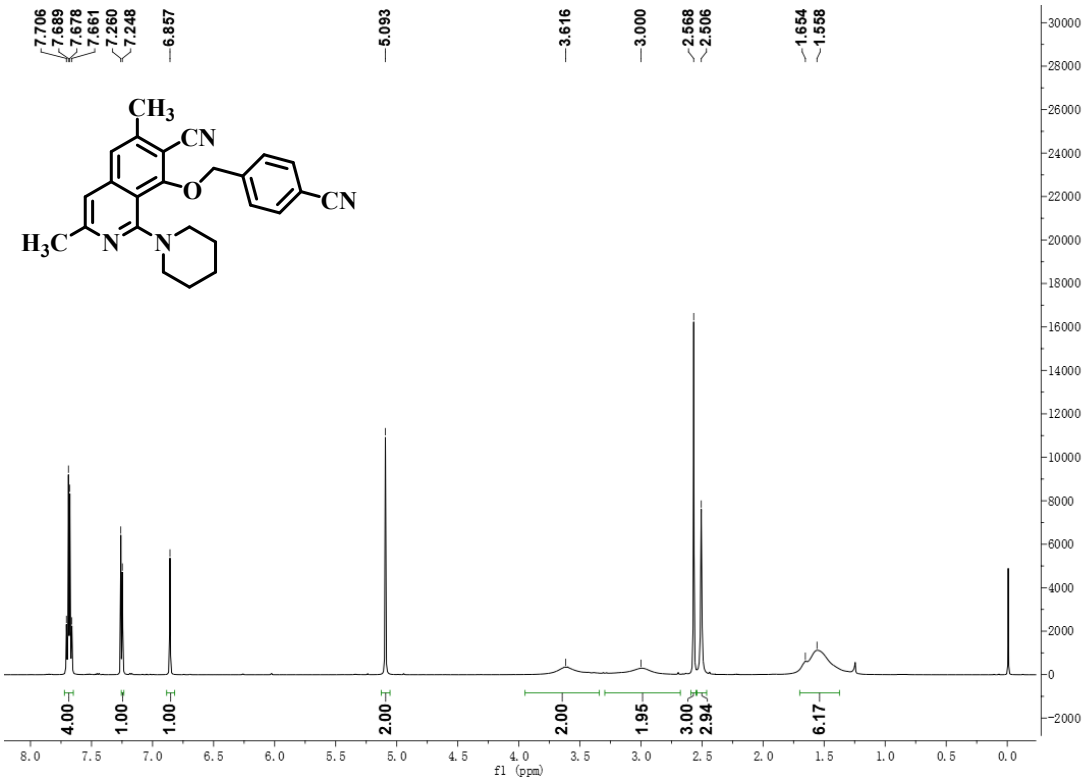

Fig. S28 ^{1}H NMR of **IQ-CN** ($CDCl_3$, 500 MHz).

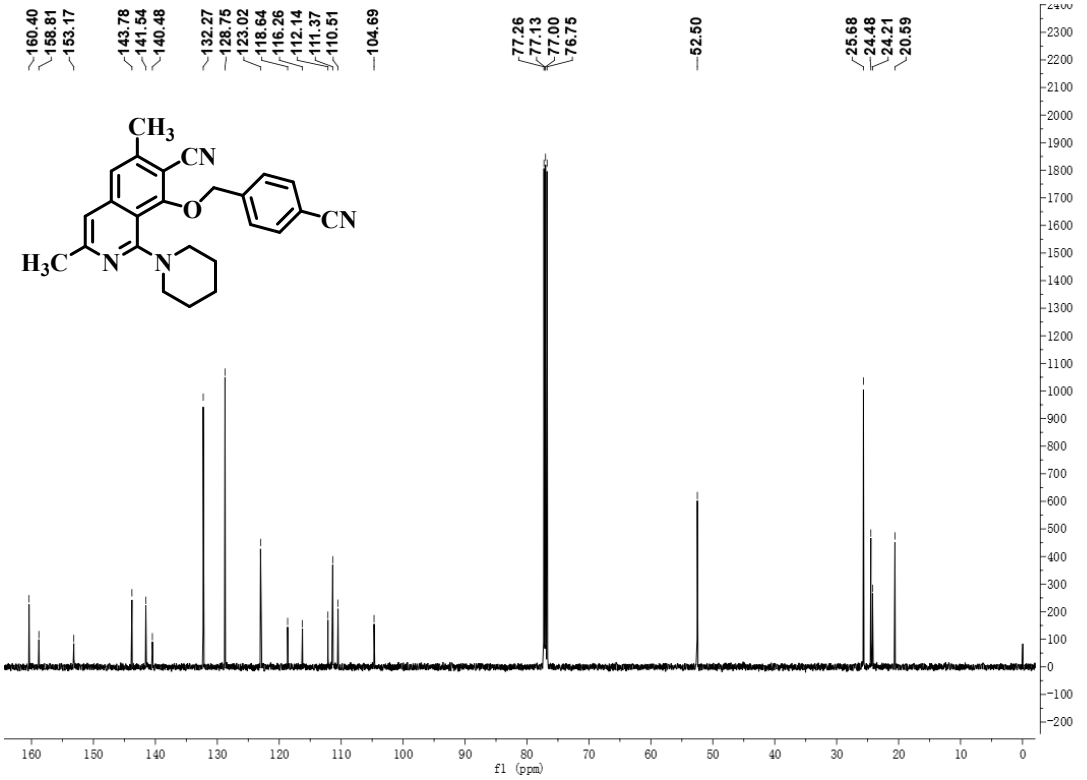

Fig. S29 ^{13}C NMR of **IQ-CN** ($CDCl_3$, 125 MHz).

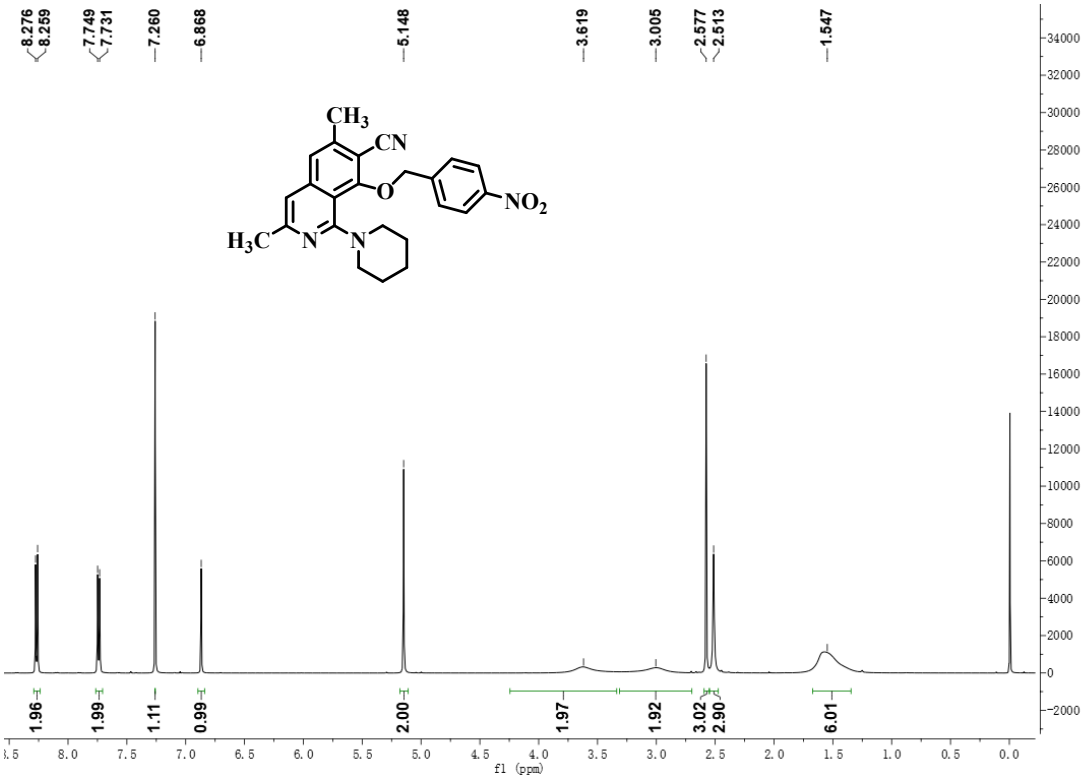

Fig. S30 ^{1}H NMR of **IQ-NO$_2$** ($CDCl_3$, 500 MHz).

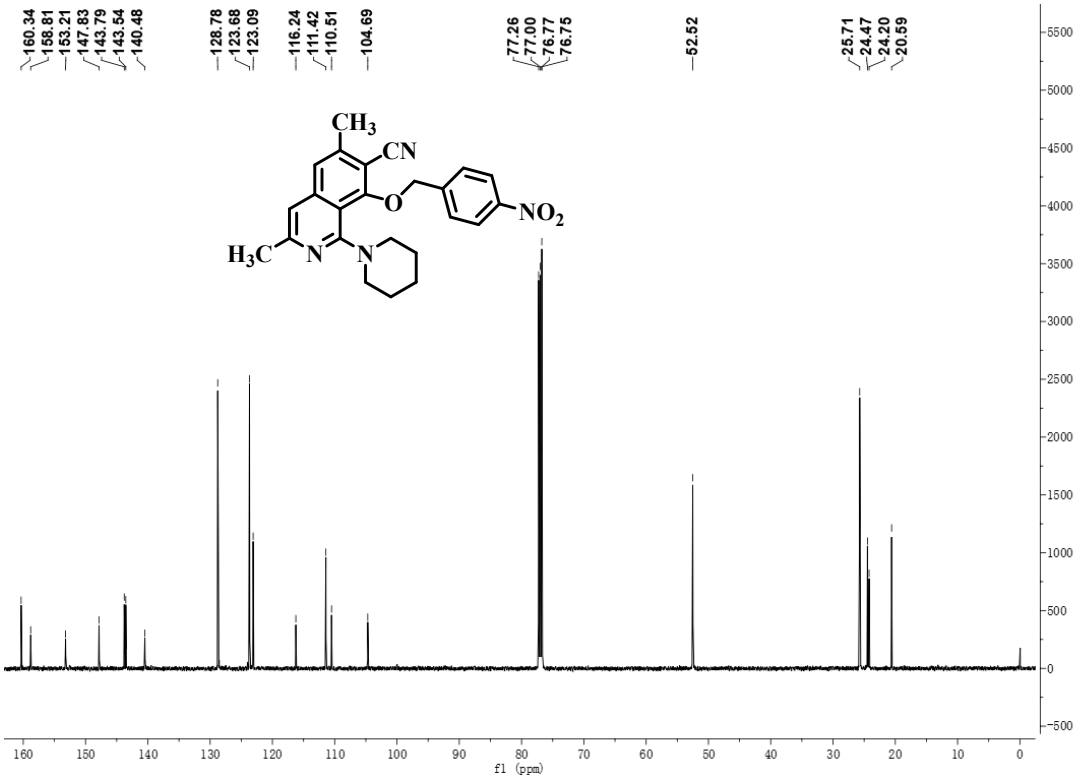

Fig. S31 ^{13}C NMR of **IQ-NO$_2$** ($CDCl_3$, 125 MHz).

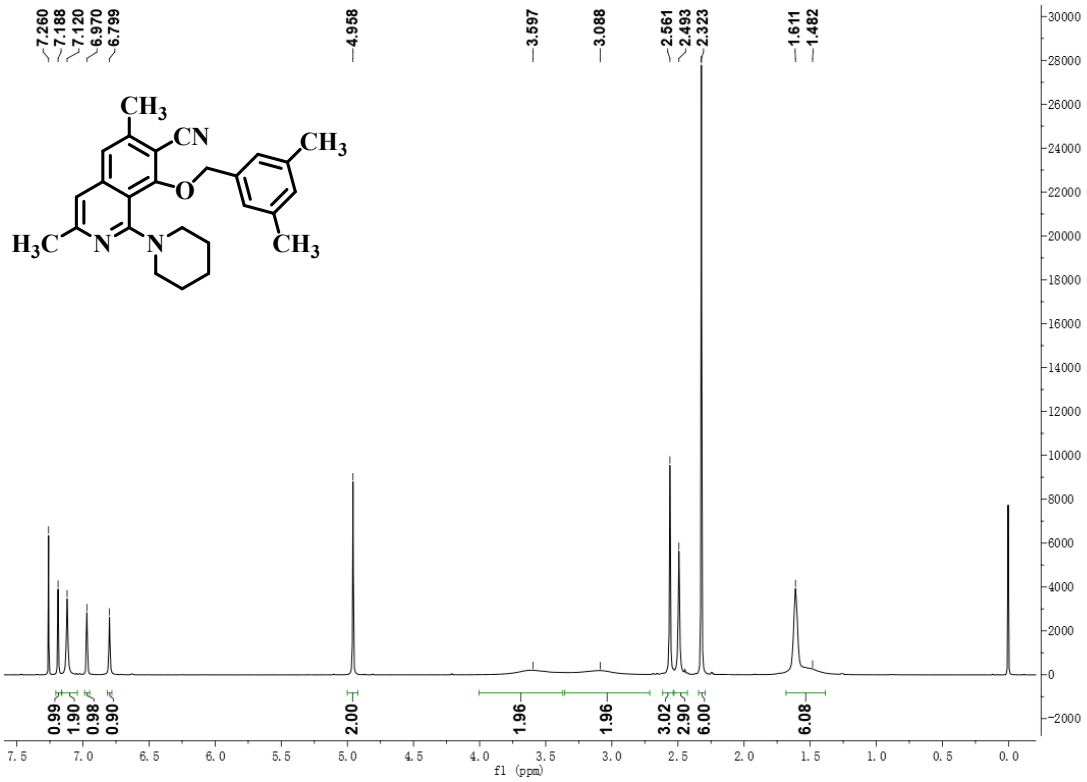

Fig. S32 ^{1}H NMR of **IQ-DMe** ($CDCl_3$, 500 MHz).

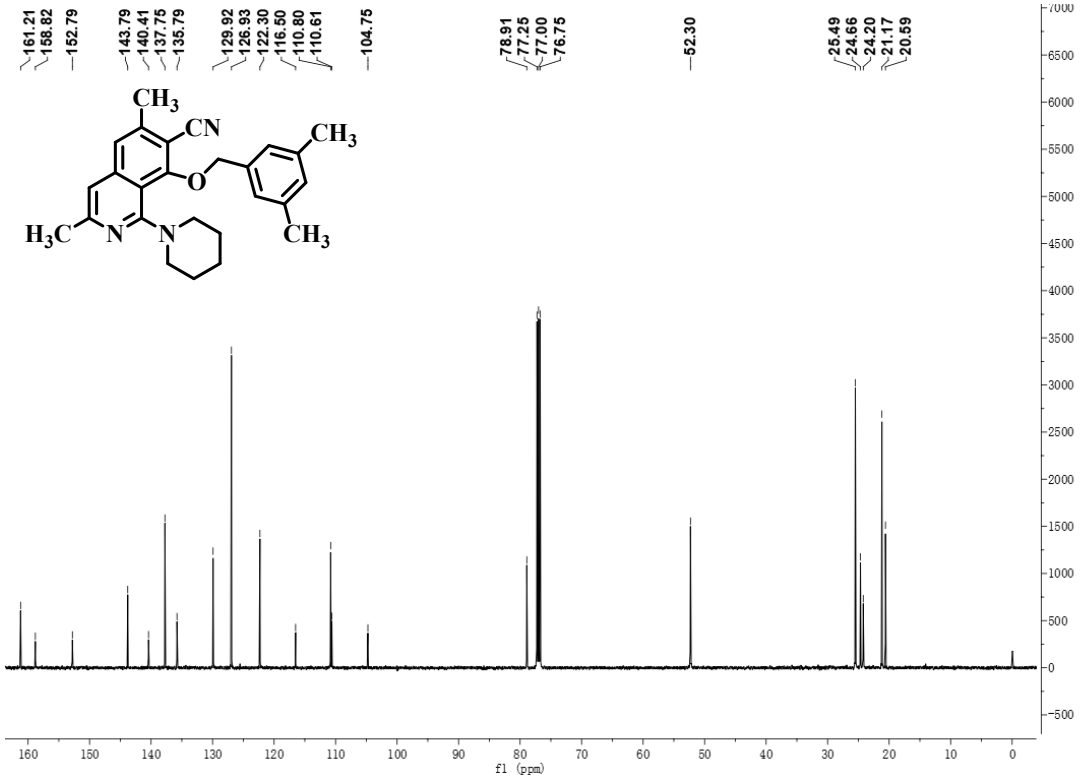

Fig. S33 ^{13}C NMR of **IQ-DMe** ($CDCl_3$, 125 MHz).

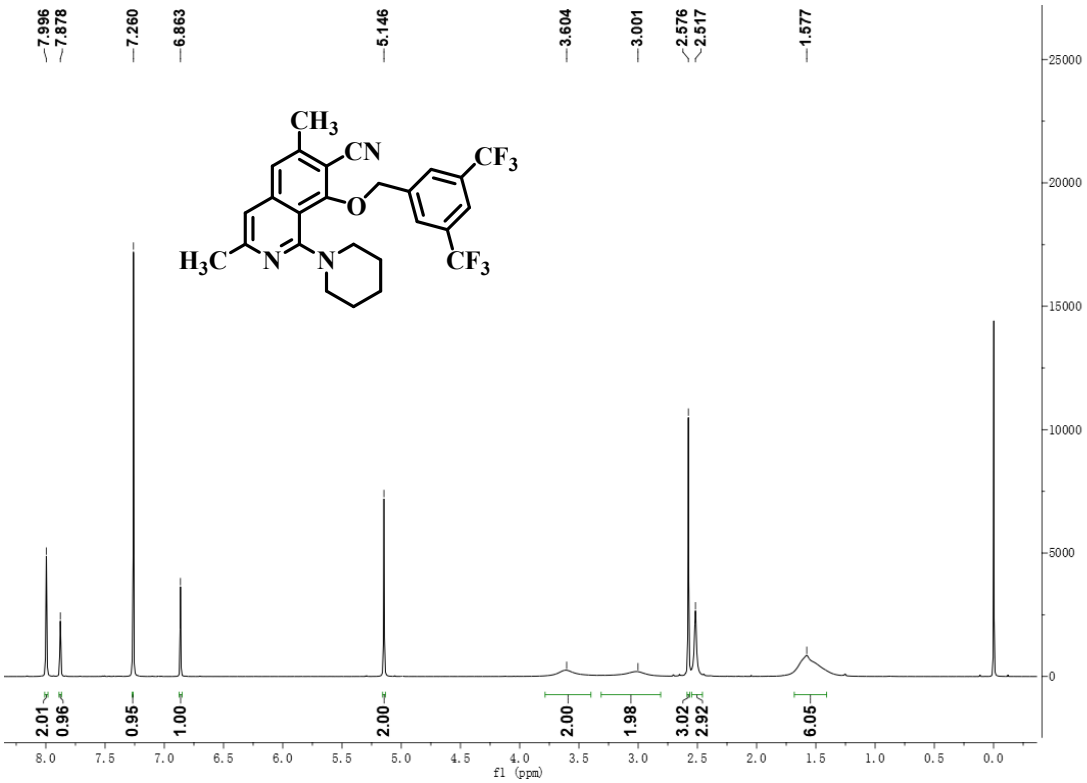

Fig. S34 ^{1}H NMR of **IQ-BTF** ($CDCl_3$, 500 MHz).

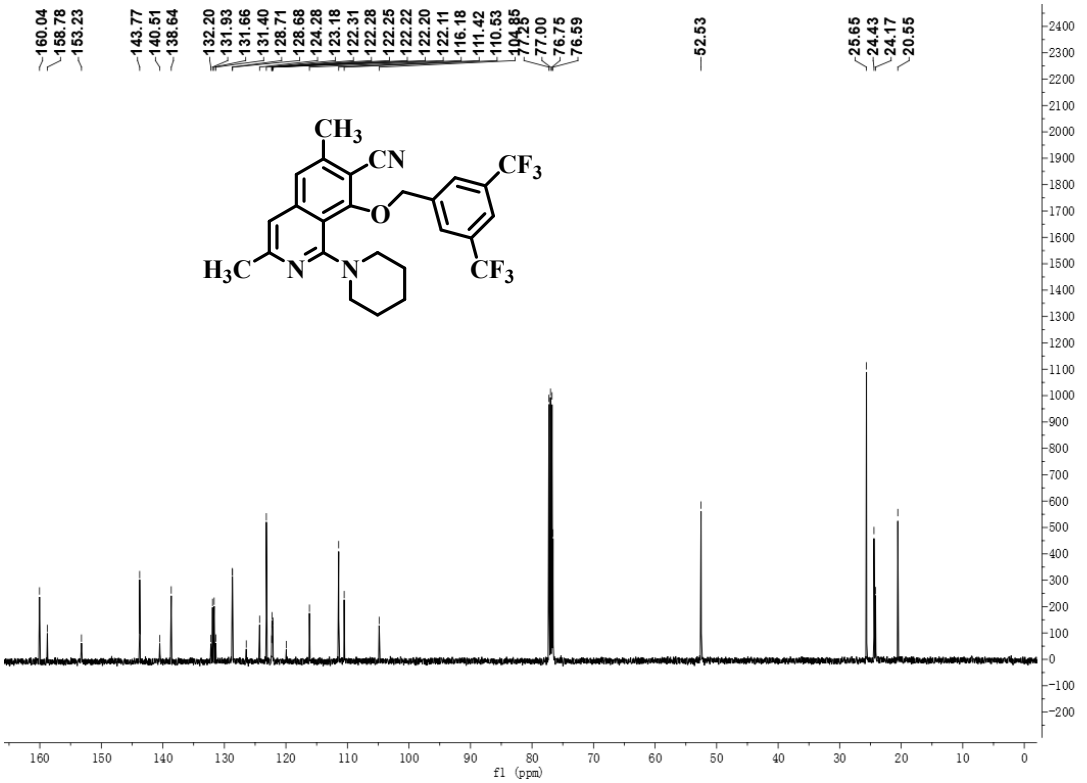

Fig. S35 ^{13}C NMR of **IQ-BTF** ($CDCl_3$, 125 MHz).