Electronic Supplementary Information

Selenium atoms induce organic doped system to produce pure phosphorescence emission

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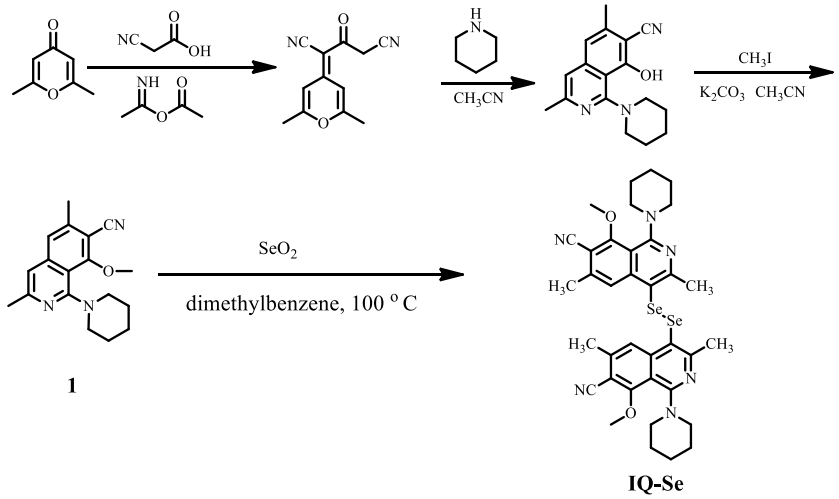
Contents:

1. Materials and characterization

All the host and guest molecules were purified by column chromatography twice, followed by recrystallization. ^1H spectra were carried out by Bruker ARX500 spectrometer with $CDCl_3$ as the solvent. Mass spectra were performed by using Finnigan BIFLEX III mass spectroscopy. UV-vis absorption spectra were measured by Persee TU-1901. Fluorescence spectra were measured by using Hitachi F-7000 spectrophotometer. Phosphorescence spectra were measured by using FLS920 lifetime and steady state spectrometer. X-ray crystal structure analyses were measured by using Bruker-AXS SMART APEX2 CCD diffractometer. Solid-state emission quantum yields were collected by using FluoroMax-4 (Horiba Jobin Yvon) fluorimeter equipped with integrated sphere. The theoretical ground-state geometry and electronic structure were performed using the density functional theory (DFT) with B3LYP hybrid functional at the basis set level of 6-31+G (d, p).

The emission quantum yields were collected by using FluoroMax-4 (Horiba Jobin Yvon) fluorimeter equipped with integrated sphere. When measuring the fluorescence quantum yields, using conventional steady-state testing methods to collect spectra. When measuring the phosphorescence quantum yields, the emission spectra of the materials were collected with a delay time of 50 us in order to filter the fluorescence emission.

2. Synthesis of the target compound



Scheme S1 Synthetic routes of the guest compound.

Synthesis of intermediate 1

The 8-methoxy-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile (**1**) was synthesized according to the previous method.[1]

Synthesis of guest IQ-Se

Intermediate compound **1** (1 mmol) and selenium dioxide (3.0 mmol) were added to the xylene (15.0 mL) solvent. The mixture was stirred for 12 h at 100 °C. After the reaction solution was cooled to room temperature, the mixture was extracted with dichloromethane. After removing the solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1, v/v) to obtain target product.

4,4'-Diselanediylbis(8-methoxy-3,6-dimethyl-1-(piperidin-1-yl)isoquinoline-7-carbonitrile) (**IQ-Se**). Light yellow solid, 68% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.00 (s, 1H), 7.75 (s, 1H), 3.88-3.86 (d, 6H), 3.72-3.21 (br, 6H), 2.65-2.38 (m, 12H), 1.72-1.61 (d, 12H) ppm.

Reference:

1. (a) Y. Chen, Y. Xie, H. S, Y. Lei, Y. Zhou, W. Dai, Z. Cai, M. Liu, X. Huang and H. Wu, *Chem. Eur. J.*, 2020, **26**, 17376-17380; (b) X. Liu, Y. Pan, Y. Lei, N. Liu, W. Dai, M. Liu, Z. Cai, H. Wu, X. Huang and Y. Dong, *J. Phys. Chem. Lett.*, 2021, **12**, 7357-7364.

3. Details of SOC theoretical calculation

SOC calculation details of **IQ-Se**

```
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tda false
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*

SOC calculation details of **IQ**

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tda false
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*

4. Figures and tables

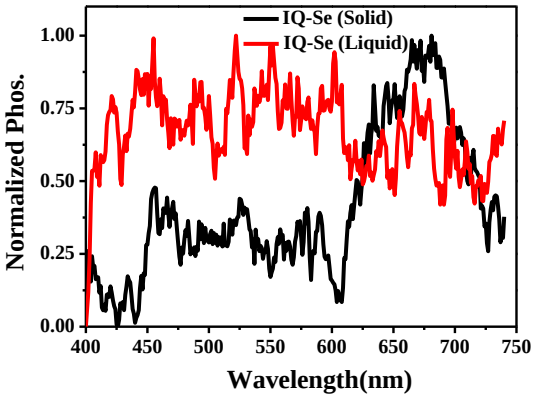

Fig. S1 Normalized fluorescence spectra of **IQ-Se** at room temperature. (Ex. = 360 nm).

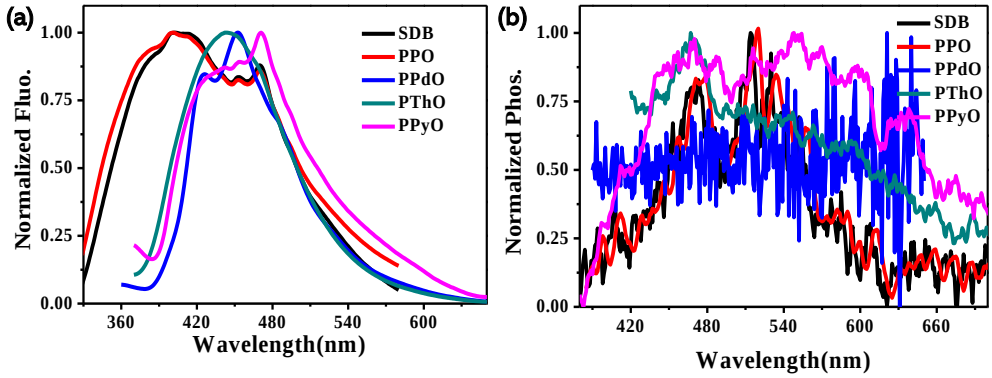

Fig. S2 (a) Normalized fluorescence spectra of five solid state hosts at room temperature. (b) Phosphorescence spectra of five solid state hosts at room temperature. (Ex. = 360 nm, Delayed time: 0.5 ms).

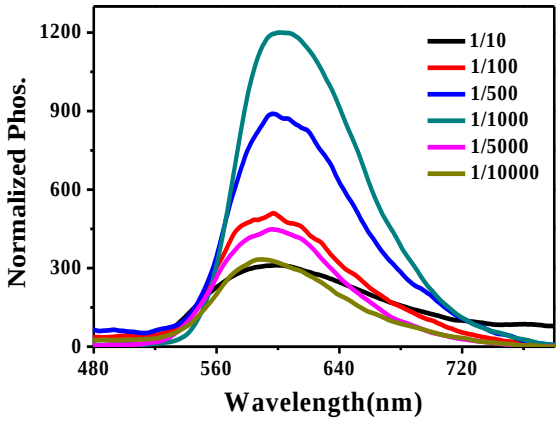

Fig. S3 Delayed emission spectra of the **IQ-Se/SDB** doped materials with different amounts of **IQ-Se** (Molar ratio). (Ex. = 360 nm, Delayed time: 0.5 ms).

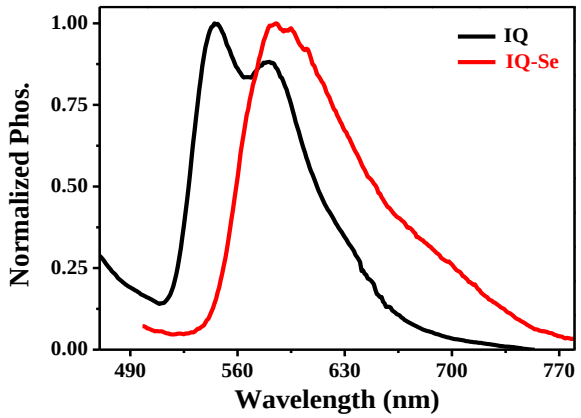

Fig. S4 Delayed emission spectra of the **IQ** and **IQ-Se** solution at 77K. (Solvent: THF; Concentration: 1.0×10^{-5} mol/L; Delayed time: 0.5 ms).

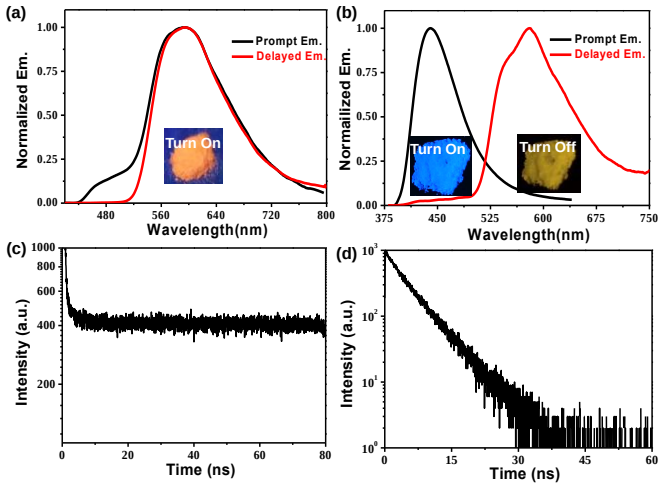

Fig. S5 (a) Prompt spectra and delayed spectra of **IQ-Se/PPO**. Inset photo: Luminous picture of **IQ-Se/PPO** under 365 nm UV lamp. (b) Prompt spectra and delayed spectra of **IQ/PPO**. Inset photo: Luminous pictures of **IQ /PPO** under different conditions. (c) Time-resolved prompt emission decay curves of **IQ-Se/PPO**. (d) Time-resolved prompt emission decay curves of **IQ/PPO**. (λ_{ex}. Phos: 360 nm, Delayed time: 0.5 ms).

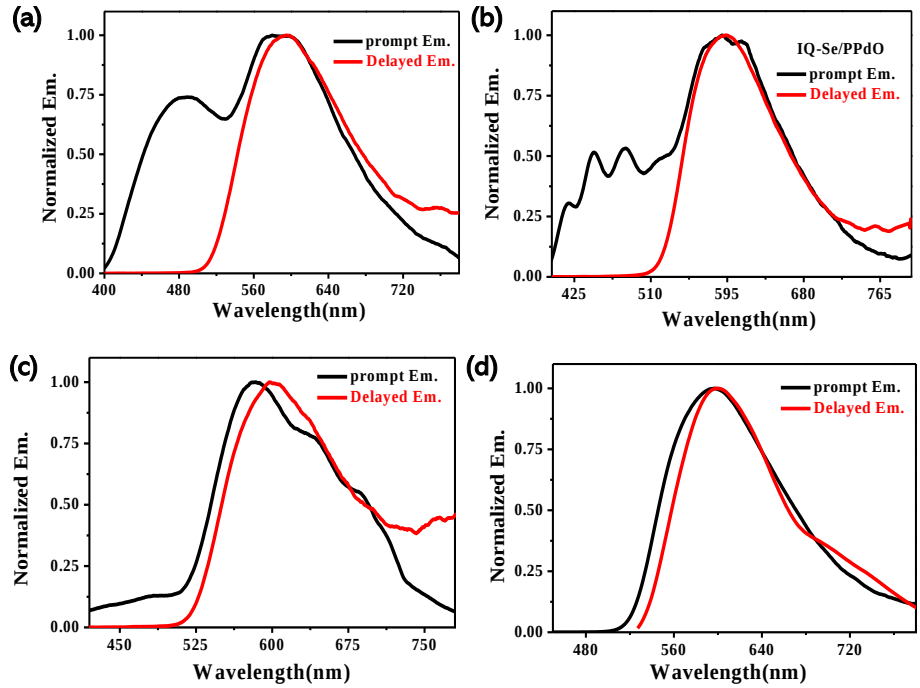

Fig. S6 Prompt spectra and delayed spectra of **IQ-Se/SDB** (a), **IQ-Se/PPyO** (b), **IQ-Se/PPdO** (c), and **IQ-Se/PThO** (d).

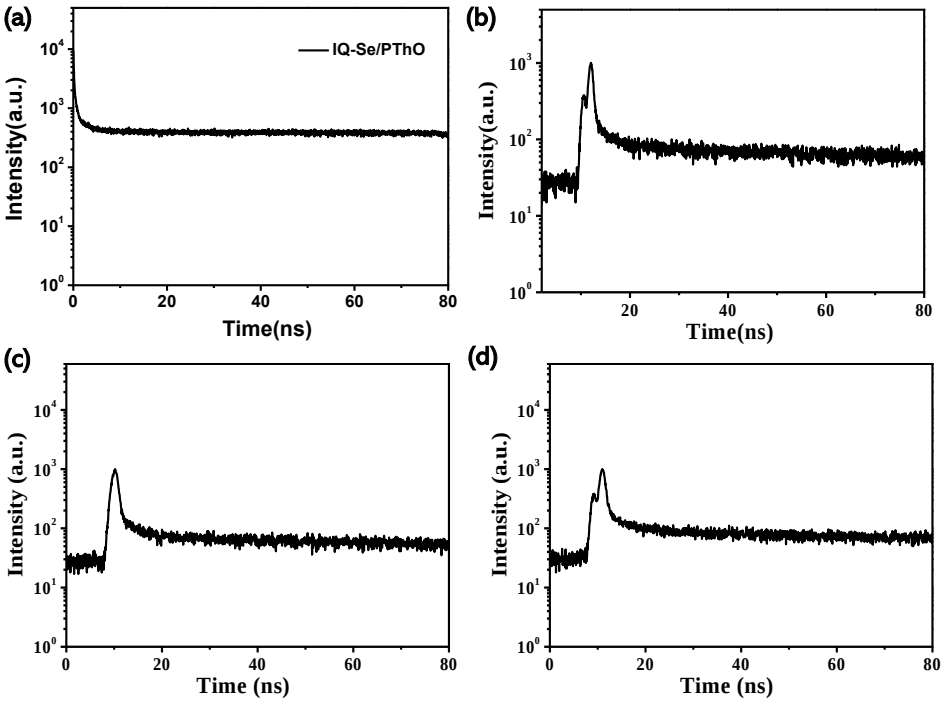

Fig. S7 Time-resolved prompt emission decay curves of **IQ-Se/SDB** (a), **IQ-Se/PPyO** (b), **IQ-Se/PPdO** (c), and **IQ-Se/PThO** (d).

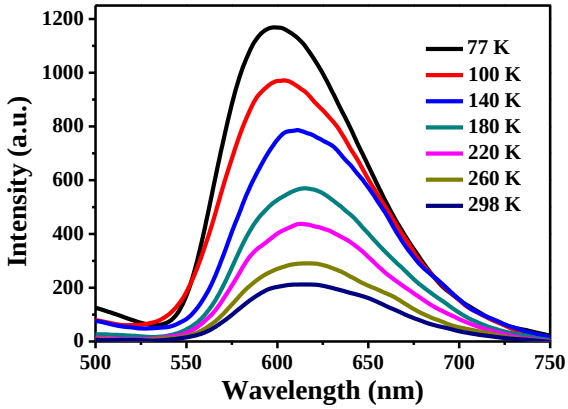

Fig. S8 Delayed spectra of **IQ-Se/PPO** at different temperatures.

Table S1 Phosphorescence properties of the doped materials

	IQ-Se/SDB	IQ-Se/PPO	IQ-Se/PPyO	IQ-Se/PPdO	IQ-Se/PThO
λ_{em} (nm)	596	600	597	601	598
τ (ms)	0.75	3.6	8.9	16.4	22.3
QY (%)	18.3	14.2	11.6	15.6	16.7

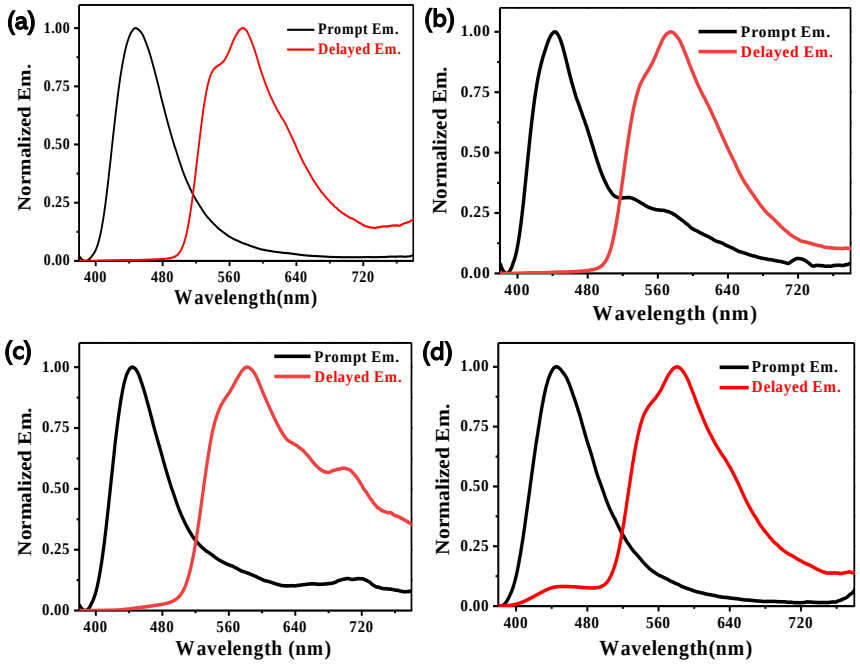

Fig. S9 Prompt spectra and delayed spectra of **IQ/SDB** (a), **IQ/PPyO** (b), **IQ/PPdO** (c), and **IQ/PThO** (d).

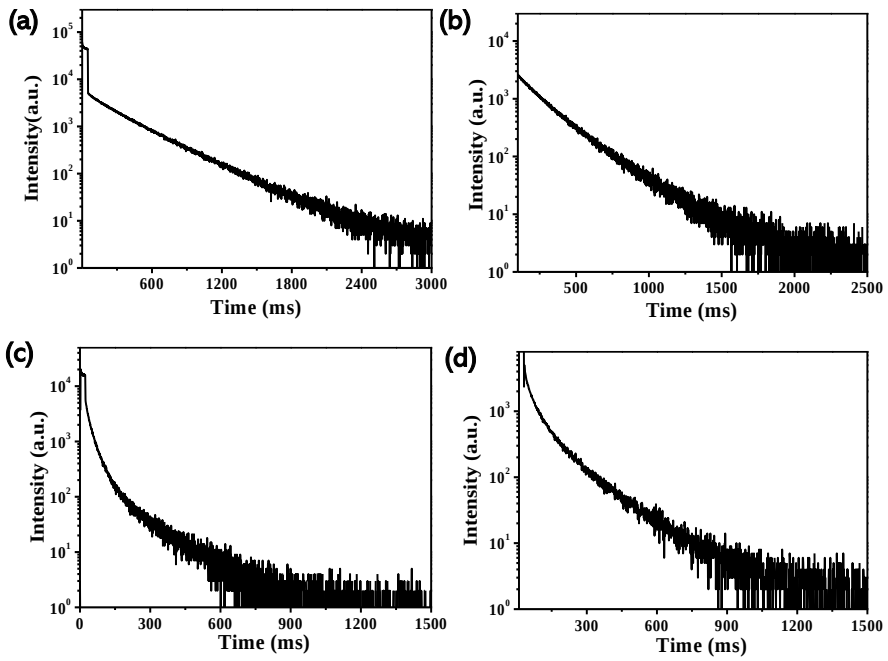

Fig. S10 Time-resolved delayed emission decay curves of **IQ/SDB** (a), **IQ/PPyO** (b), **IQ/PPdO** (c), and **IQ/PThO** (d).

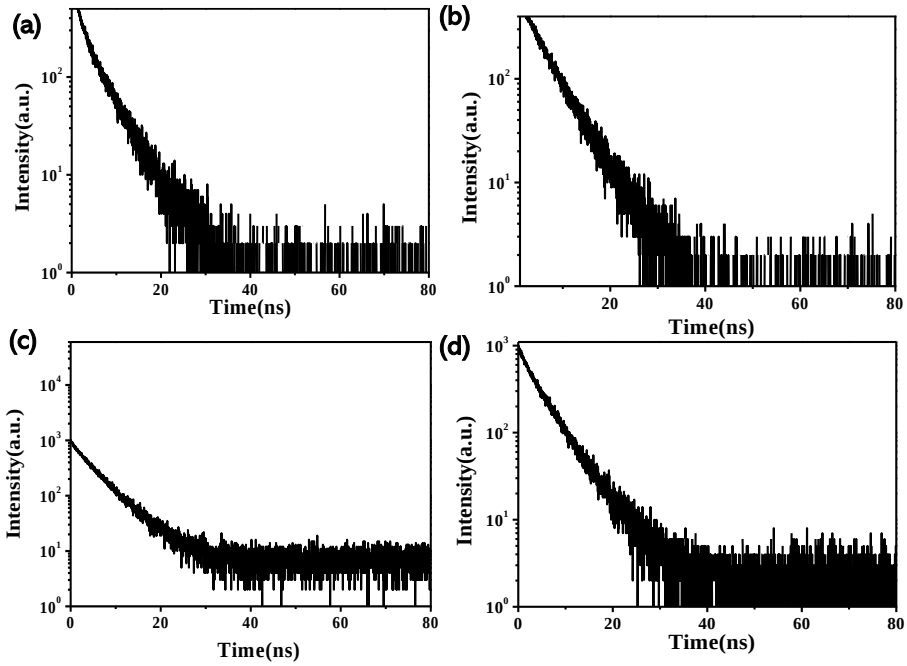

Fig. S11 Time-resolved prompt emission decay curves of **IQ/SDB** (a), **IQ/PPyO** (b), **IQ/PPdO** (c), and **IQ/PThO** (d).

Table S2. Photophysical properties of the doped materials

	IQ/SDB	IQ/PPO	IQ/PPyO	IQ/PPdO	IQ/PThO
$\tau_{Fluo.}$ (ns)	1.85	2.13	2.32	2.34	2.10
$\tau_{Phos.}$ (ms)	224	187	165	103	87
QY. $_{Phos.}$ (%)	11.7	15.2	7.8	13.5	8.4
QY. $_{Fluo.}$ (%)	35.6	28.7	32.4	26.6	33.8

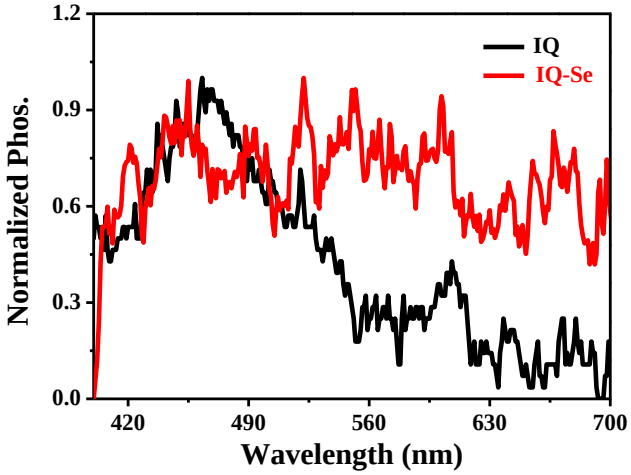

Fig. S12 Normalized phosphorescence spectra of **IQ** and **IQ-Se** at room temperature. (Ex. = 360 nm; Delayed time: 50 us).

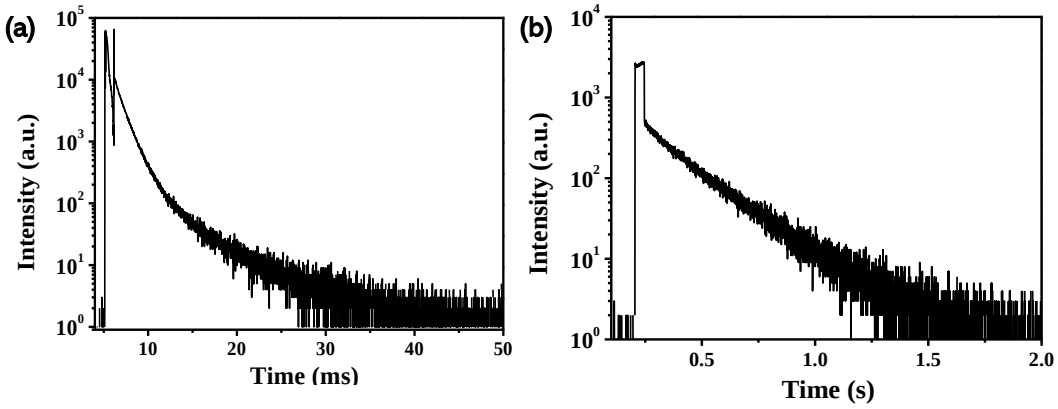

Fig. S13 Time-resolved delayed emission decay curves of **IQ-Se** (a) and **IQ** (b) at room temperature (77 K).

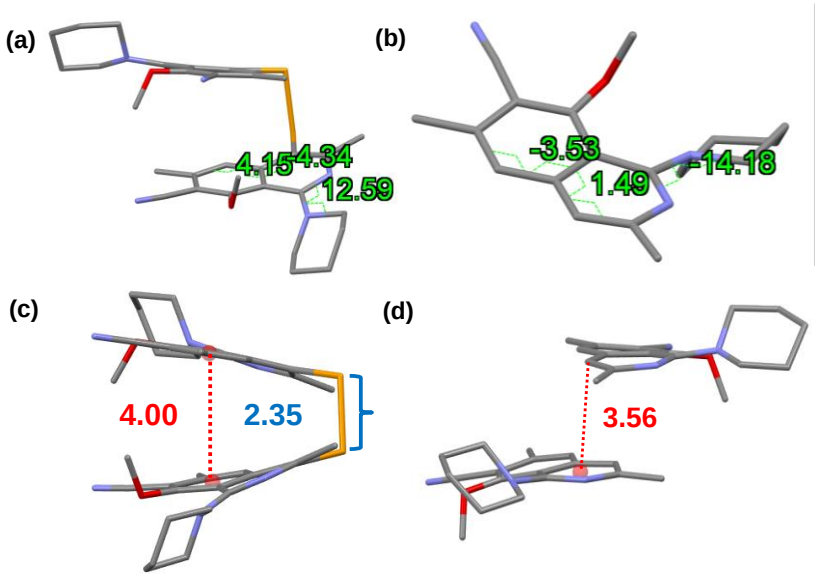

Fig. S14 (a) Molecular configuration of single crystal **IQ-Se**. (b) Molecular configuration of single crystal **IQ**. (c) Intramolecular effective distance of single crystal **IQ-Se**. (d) Intermolecular effective distance of single crystal **IQ**.

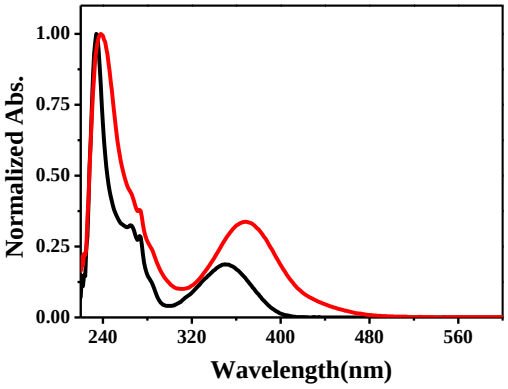

Fig. S15 UV absorption spectra **IQ** and **IQ-Se** in solution state.

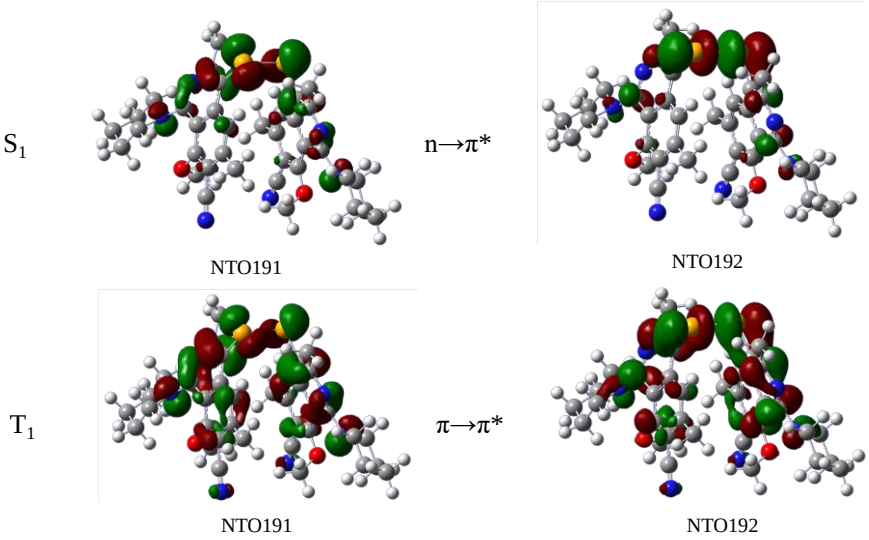

Fig. S16. Natural transition orbits (NTO) of the singlet and triplet states of the **IQ-Se**.

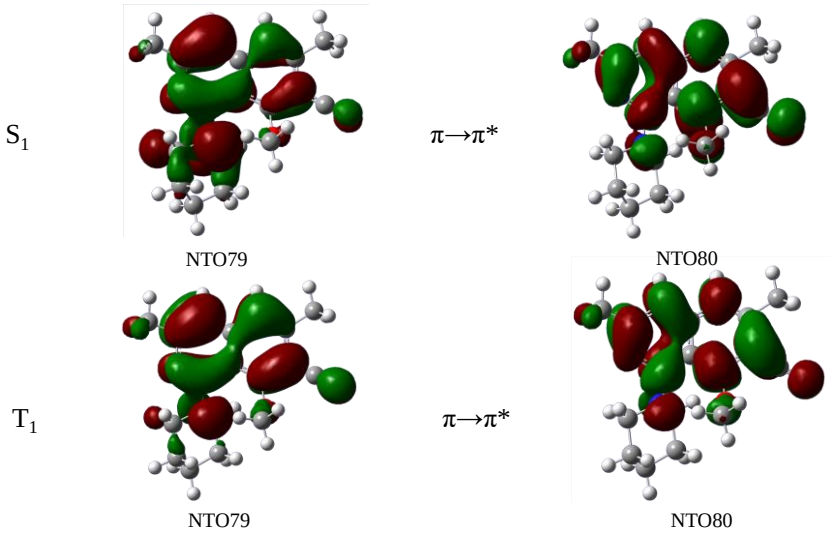

Fig. S17. Natural transition orbits (NTO) of the singlet and triplet states of the **IQ**.

As shown in Fig. S18, the maximum wavelength of **SDB** is 298 nm, while that of **IQ-Se** is 370 nm. Next, the phosphorescence emission of **IQ-Se/SDB** at different excitation wavelengths were investigated, the results showed that the phosphorescence intensity at the excitation wavelength of 370 nm is much stronger than that at the excitation wavelength of 300 nm (Fig. S17). Furthermore, even if the excitation wavelength extends to 420 nm, in which **SDB** hardly absorbs the energy of this band, the doped material still shows phosphorescence emission (Fig. S17). These results clearly demonstrate that the phosphorescence should come from the energy absorbed by the guest molecules. We have tried to test the UV transient absorption of doped materials, but the current test is mainly for samples in solution. The requirements for solid samples are too harsh and it is difficult to obtain valid data. But in future work, we will work hard to study the in-depth luminescence mechanism of doped materials.

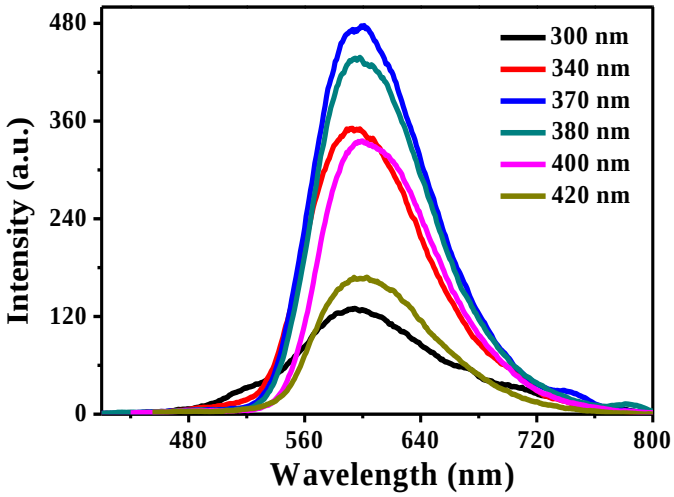

Fig. S18. Delayed emission spectra of **IQ-Se/SDB** under different excitation wavelengths.

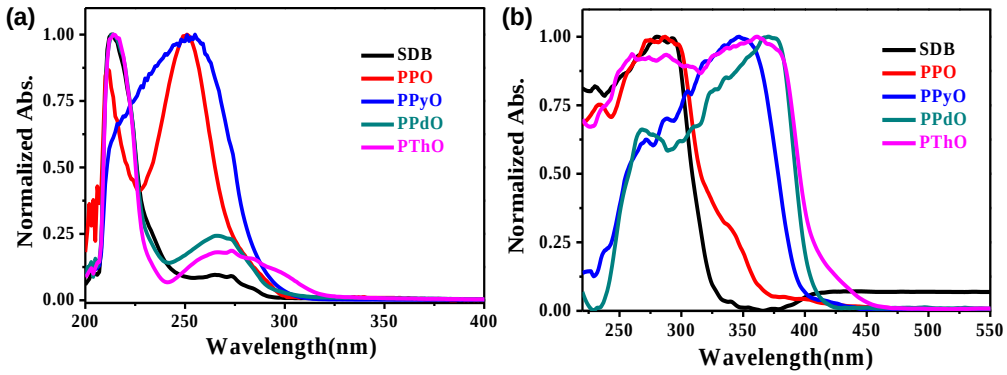

Fig. S19 UV absorption spectra of five hosts in solution state (a) and solid state (b).

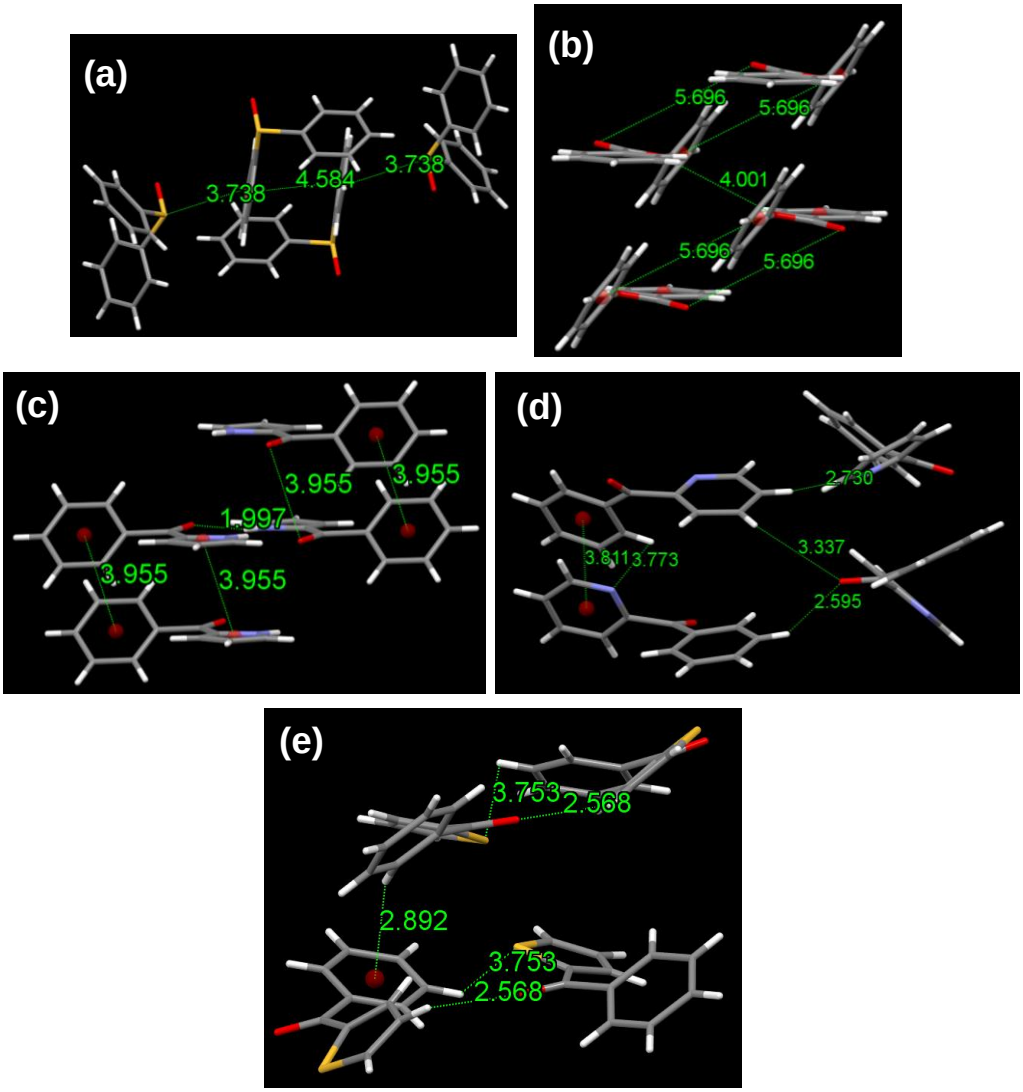

Fig. S20 Single crystal of **SDB** (a), **PPO** (b), **PPyO** (c), **PPdO** (d), and **PThO** (e).

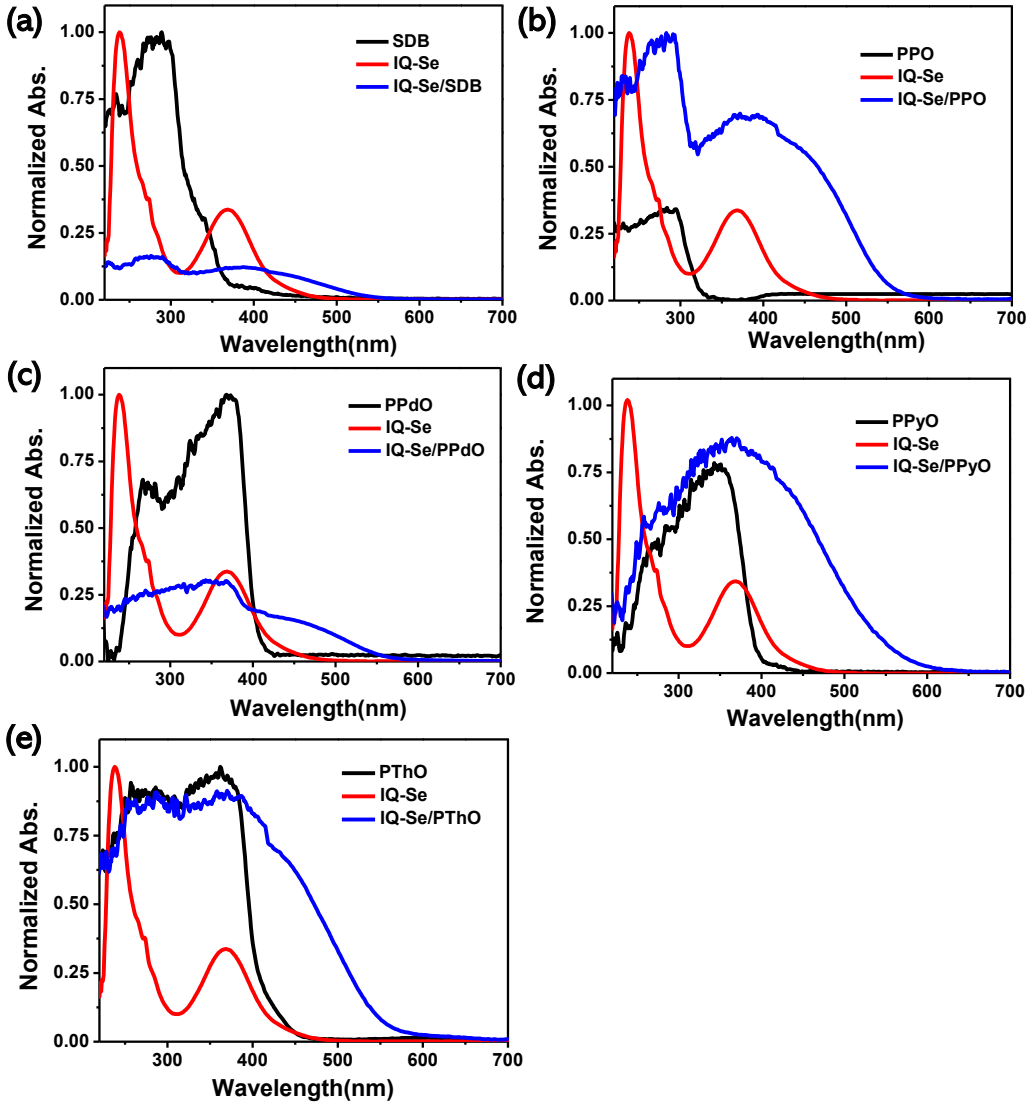

Fig. S21 Absorption wavelengths of the guest, hosts and doped materials

Table S3. Crystal data of guest and five hosts.

	IQ-Se	**SDB**	**PPO**	**PPdO**	**PThO**	**PPyO**
CCDC (NO.)	2120642	2098103	2121526	2086860	2121522	2121523
Empirical formula	$C_{36}H_{40}N_6O_2Se_2$	$C_{12}H_{10}OS$	$C_{13}H_{10}O_2$	$C_{12}H_9NO$	$C_{11}H_8OS$	$C_{11}H_9NO$
Formula weight	746.66	202.26	198.21	183.20	188.23	171.19
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	C 2/c	P 21/n	P 21/c	P 21 21 21	P 21 21 21	P -1
Z	8	4	4	4	4	2
Dcalcd [Mg/m^3]	1.432	1.299	1.287	1.280	1.334	1.313
F (000)	3056	424	416	384	392	180
θ range [°]	2.572-25.997°	2.736-25.991°	2.761-25.996°	3.071-26.000°	3.161-25.989°	2.993-25.999°
R_1 [I>2σ(I)]	0.0330	0.0389	0.0368	0.0342	0.0337	0.0409
wR_2 [I>2σ(I)]	0.0774	0.0849	0.0907	0.0799	0.0841	0.0981
a [Å]	37.8827(10)	8.3623(15)	5.6958(4)	8.055(4)	7.6504(4)	3.9549(4)
b [Å]	8.5799(3)	14.109(2)	14.7552(10)	10.096(6)	10.2520(5)	10.6225(13)
c [Å]	21.8681(6)	8.9317(18)	12.4061(10)	11.687(5)	11.9536(5)	10.6802(11)
α [deg]	90	90	90	90	90	98.127(4)
β [deg]	103.0210(10)	101.138(7)	101.086(2)	90	90	98.311(3)
γ [deg]	90	90	90	90	90	98.368(4)
V [$Å^3$]	6925.0(4)	1034.0(3)	1023.19(13)	950.5(9)	937.54(8)	433.16(8)
GOF	1.035	1.039	1.040	1.035	1.070	1.053
R(int)	0.0503	0.0366	0.0245	0.0326	0.0218	0.0366
No. of reflcns collected	34082	10955	11579	7946	4627	5986
No. of unique reflcns	6779	2031	1982	1845	1812	1690
R_1 (all data)	0.0517	0.0539	0.0444	0.0404	0.0382	0.0577
wR_2 (all data)	0.0863	0.0955	0.0974	0.0845	0.0879	0.1100

5. NMR Spectra

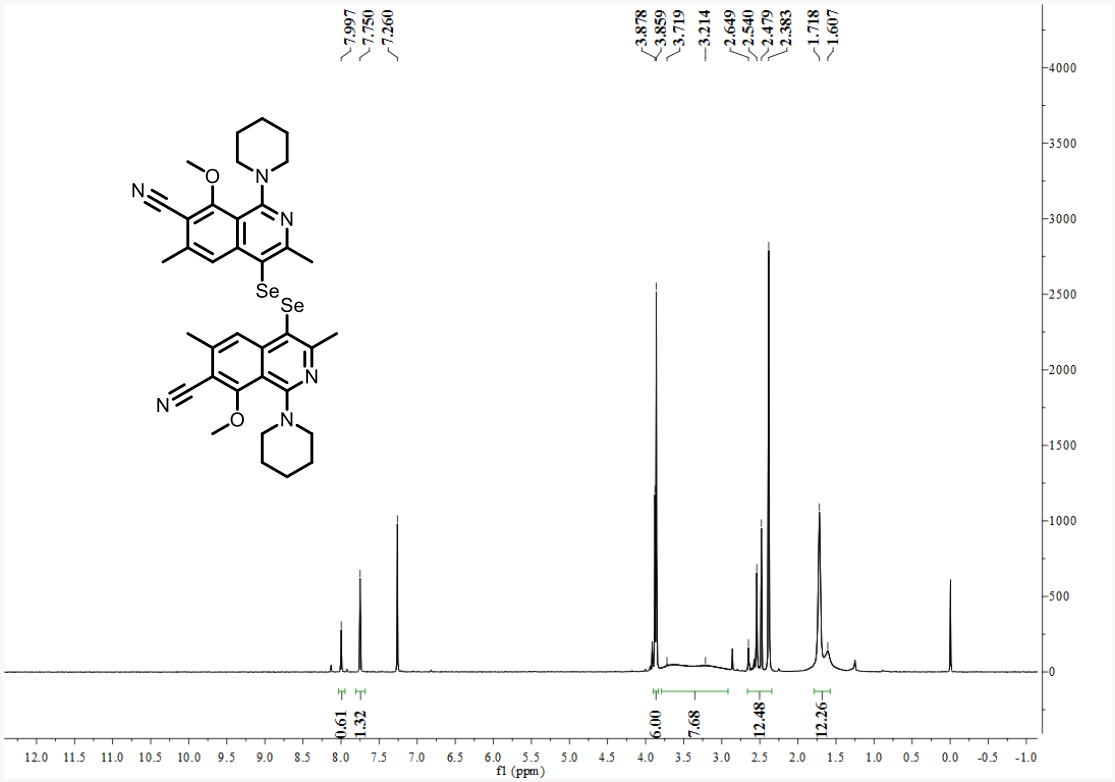

Fig. S22 ^{1}H NMR spectra of **IQ-Se** ($CDCl_3$, 500 MHz).

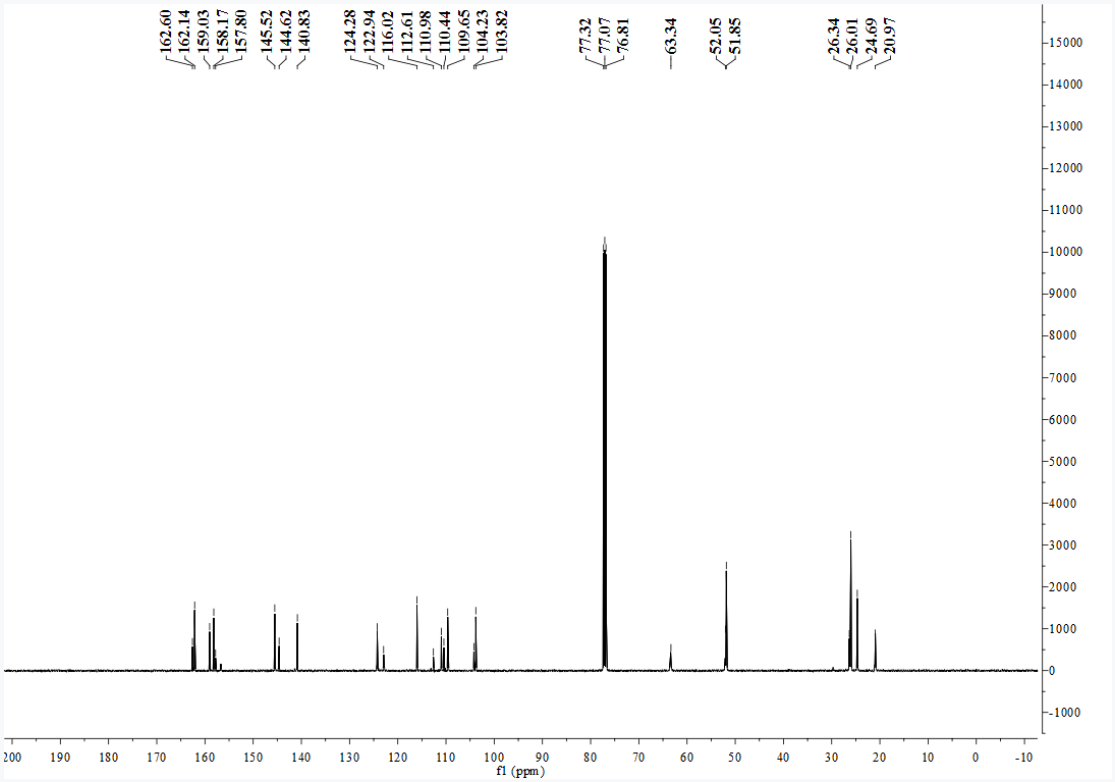

Fig. S23 ^{13}C NMR spectra of **IQ-Se** ($CDCl_3$, 125 MHz).