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Supporting Information

Third-order nonlinear optical properties of axially modified indium phthalocyanine with alkyl chain

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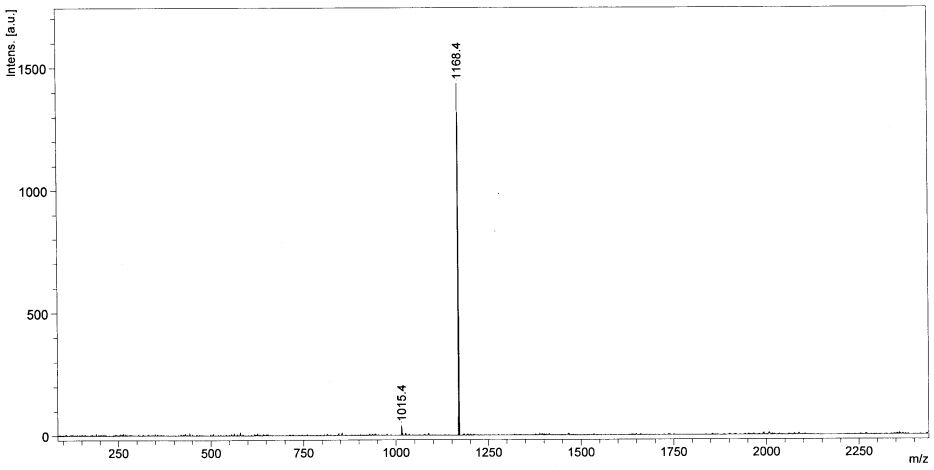

Fig. S1 The MALDI-TOF MS spectrum of (**InClPc**, **4**).

The MALDI-TOF MS spectrum spectra of (**InClPc**, **4**) is shown in the **Fig. S1**. 1168.4 corresponds to the molecular weight of Cl removed from (**InClPc**, **4**), and (**InClPc**, **4**) is combined with CCA. The value corresponding to (**InClPc**, **4**) is 1015.4. This value corresponds the molecular weight of (**InClPc**, **4**).

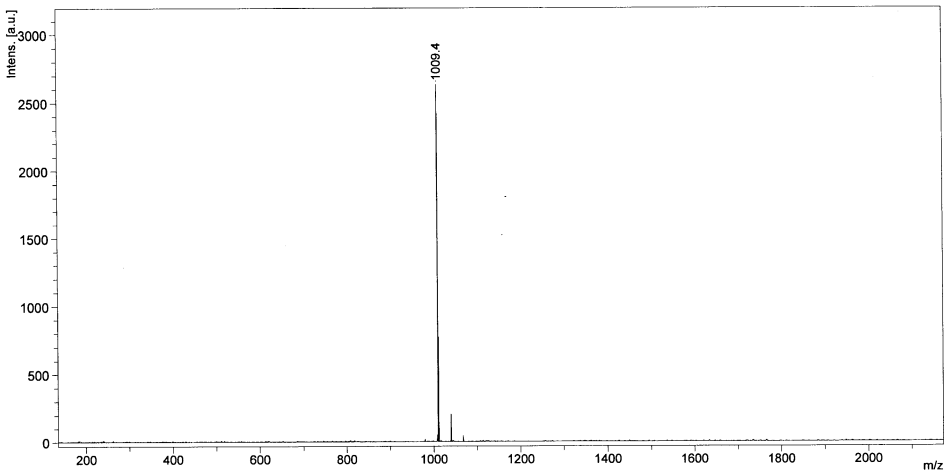

Fig. S2 The MALDI-TOF MS spectrum of (**(C_2)InPc**, **5**).

The MALDI-TOF MS spectrum spectra of (**(C_2)InPc**, **5**) is shown in the **Fig. S2**. 1009.4 corresponds to the molecular weight of [**(C_2)InPc** + H]$^+$.

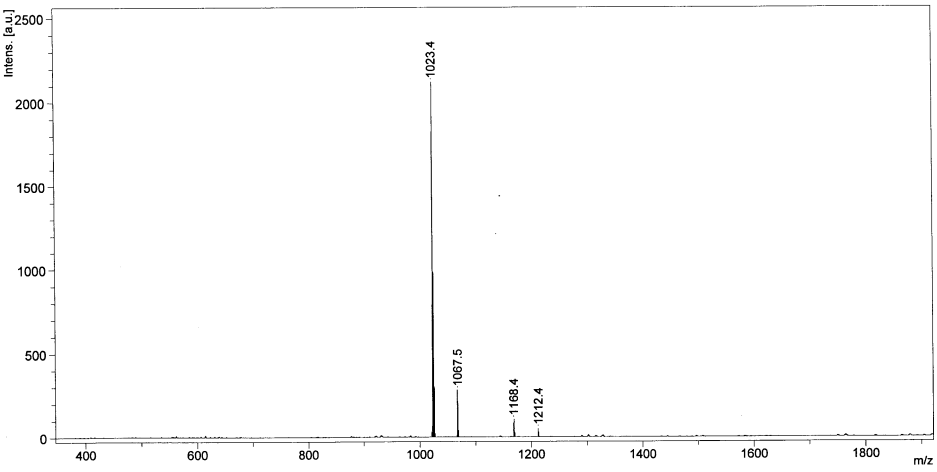

Fig. S3 The MALDI-TOF MS spectrum of (**(C_3)InPc**, **6**)

The MALDI-TOF MS spectrum spectra of (**(C_3)InPc**, **6**) is shown in the **Fig. S3**. 1023.4 corresponds to the molecular weight of [**(C_3)InPc** + H]$^+$, and 1067.5 corresponds to the molecular weight of [**(C_3)InPc** + [C_3H_7]$^+$]. 1168.4 corresponds to the molecular weight of [**InClPc**$^+$ + CCA], and 1212.4 corresponds to the molecular weight of [**(C_3)InPc** + CCA].

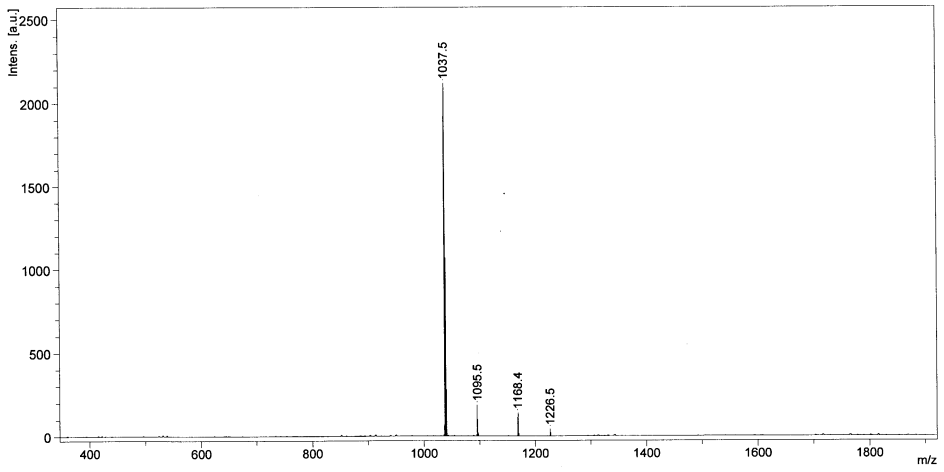

Fig. S4 The MALDI-TOF MS spectrum of (**(C_4)InPc**, **7**).

The MALDI-TOF MS spectrum spectra of (**(C_4)InPc**, **7**) is shown in the **Fig. S4**. 1037.5 corresponds to the molecular weight of [**(C_4)InPc** + H]$^+$, and 1095.5 corresponds to the molecular weight of [**(C_4)InPc** + [C_4H_9]$^+$]. 1168.4 corresponds to the molecular weight of [**InClPc** $^+$ + CCA], and 1226.5 corresponds to the molecular weight of [**(C_4)InPc** + CCA].

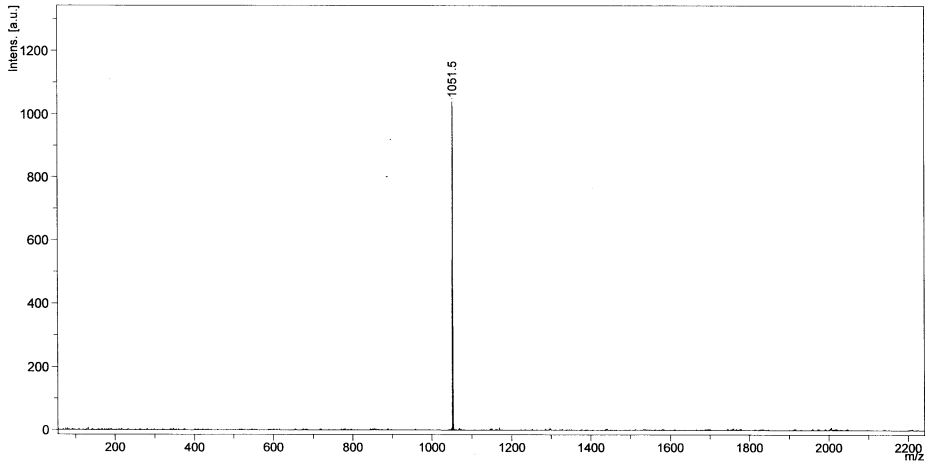

Fig. S5 The MALDI-TOF MS spectrum of (**(C_5)InPc**, **8**).

The MALDI-TOF MS spectrum spectra of (**(C_5)InPc**, **8**) is shown in the **Fig. S5**. 1051.5 corresponds to the molecular weight of [**(C_5)InPc** + H]$^+$.

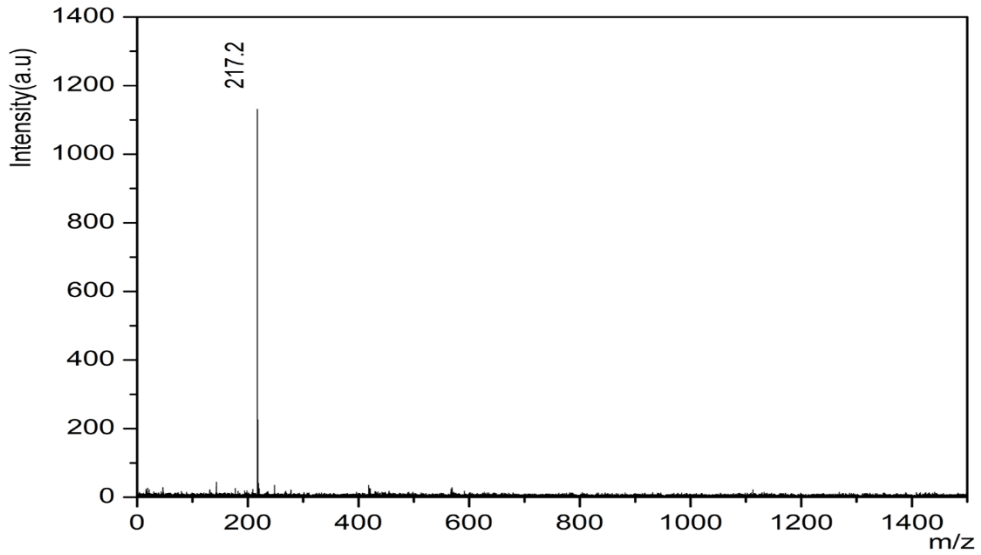

Fig. S6 The MALDI-TOF MS spectrum of phthalonitrile (**3**).

The MALDI-TOF MS spectrum spectra of phthalonitrile (**3**) is shown in the **Fig. S6**. 217.2 corresponds to the molecular weight of [**3** + H]$^+$.

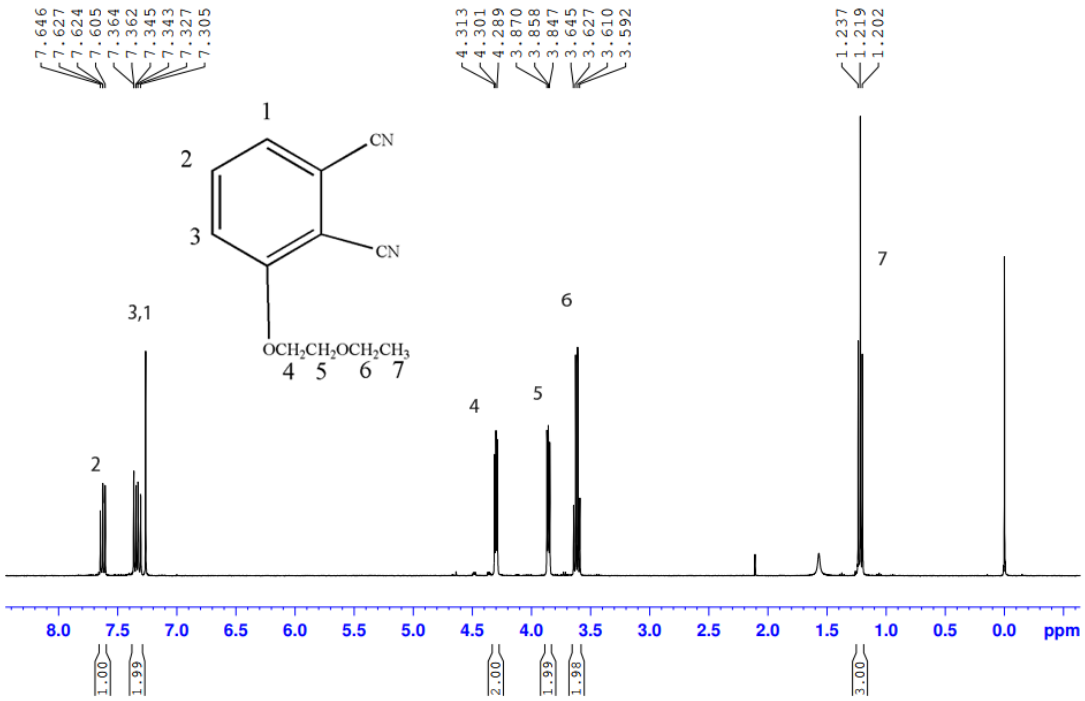

Fig. S7 ^{1}H NMR spectrum of tetra-[3-(2-ethoxy)ethoxy] phthalonitrile (**3**).

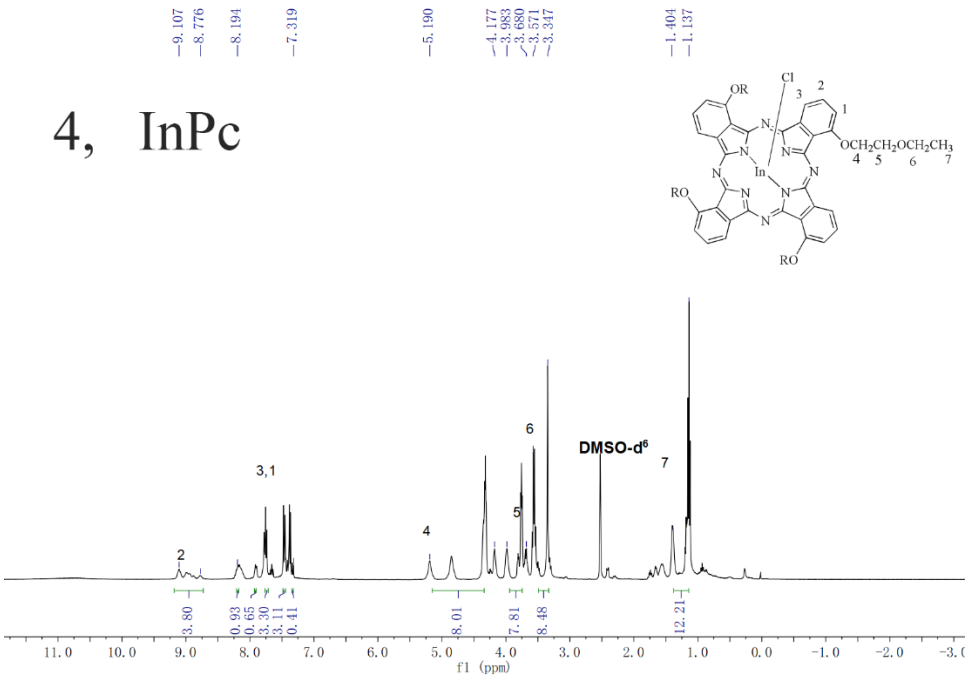

Fig. S8 ^{1}H NMR spectrum of (**InClPc**, **4**).

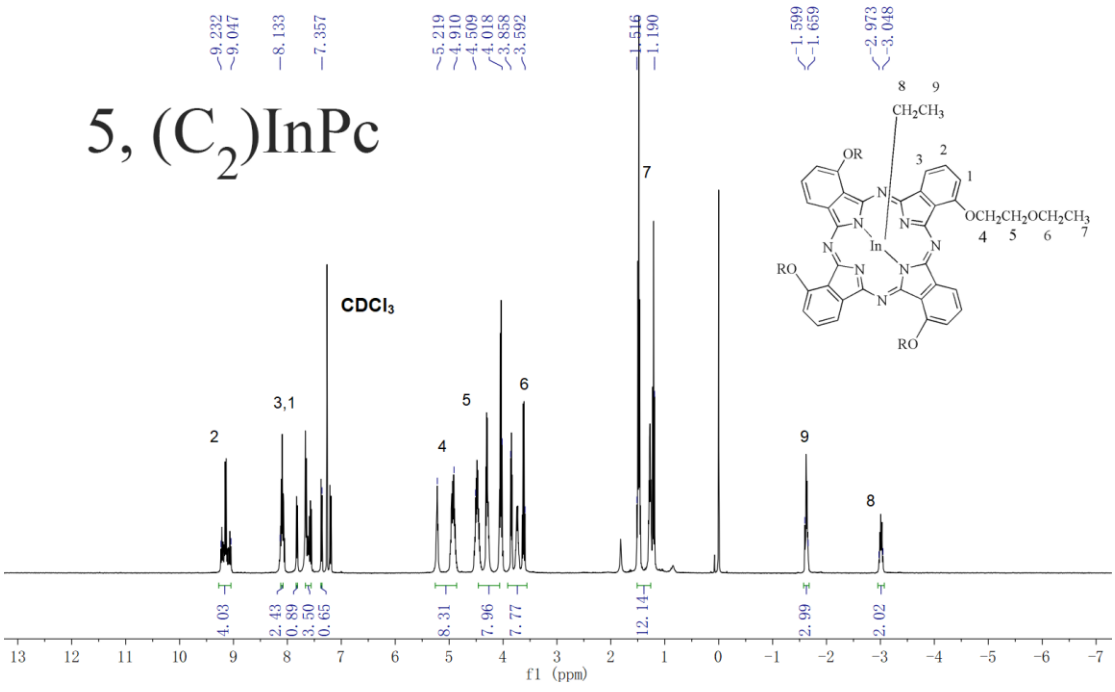

Fig. S9 ^{1}H NMR spectrum of (**(C_2)InPc**, **5**).

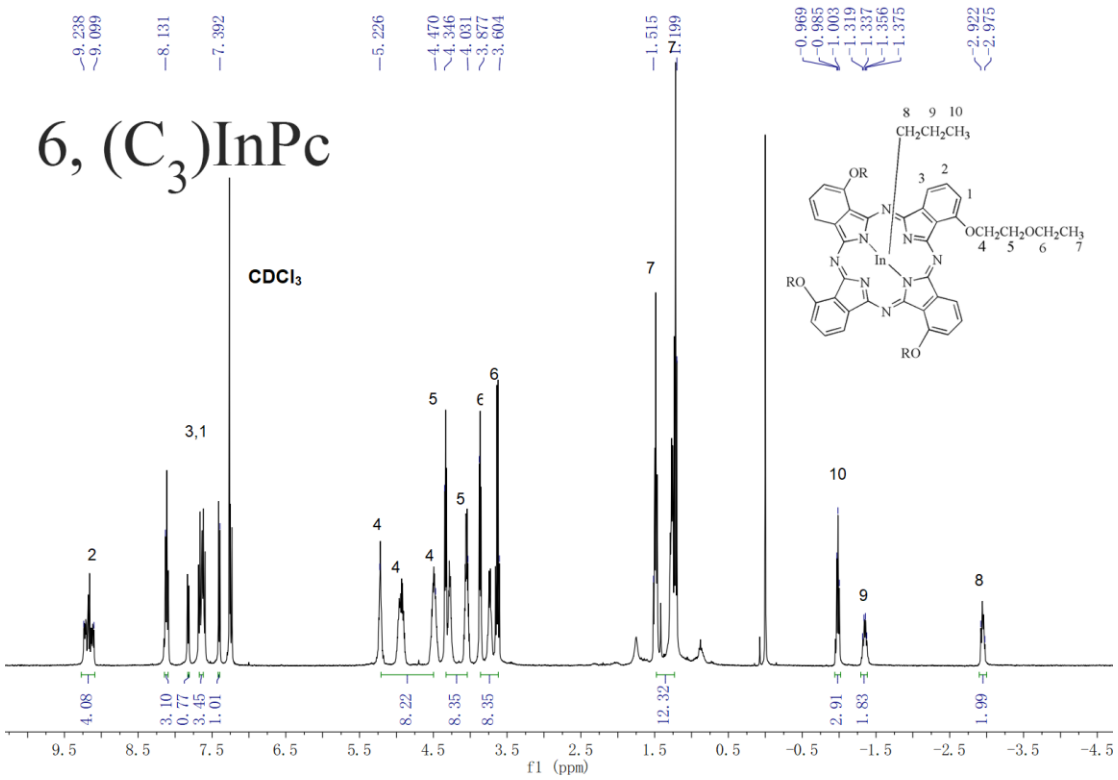

Fig. S10 ^{1}H NMR spectrum of (**(C_3)InPc**, **6**).

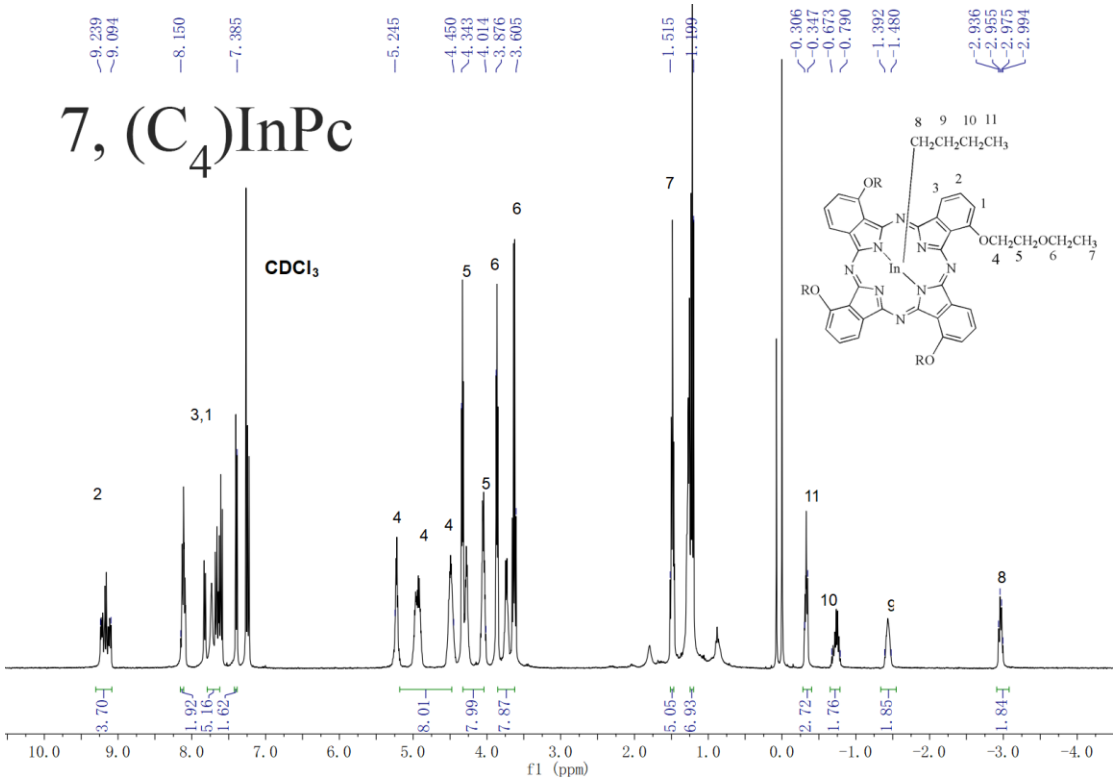

Fig. S11 ^{1}H NMR spectrum of (**(C_4)InPc**, **7**).

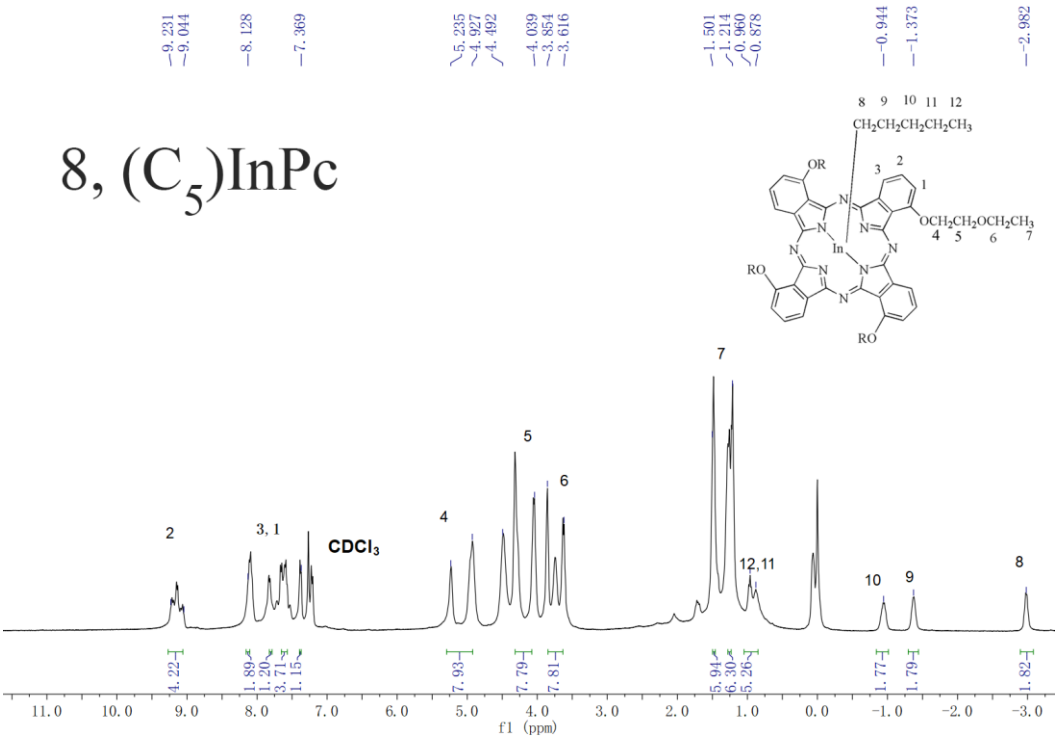

Fig. S12 ^{1}H NMR spectrum of (**(C_5)InPc**, **8**).

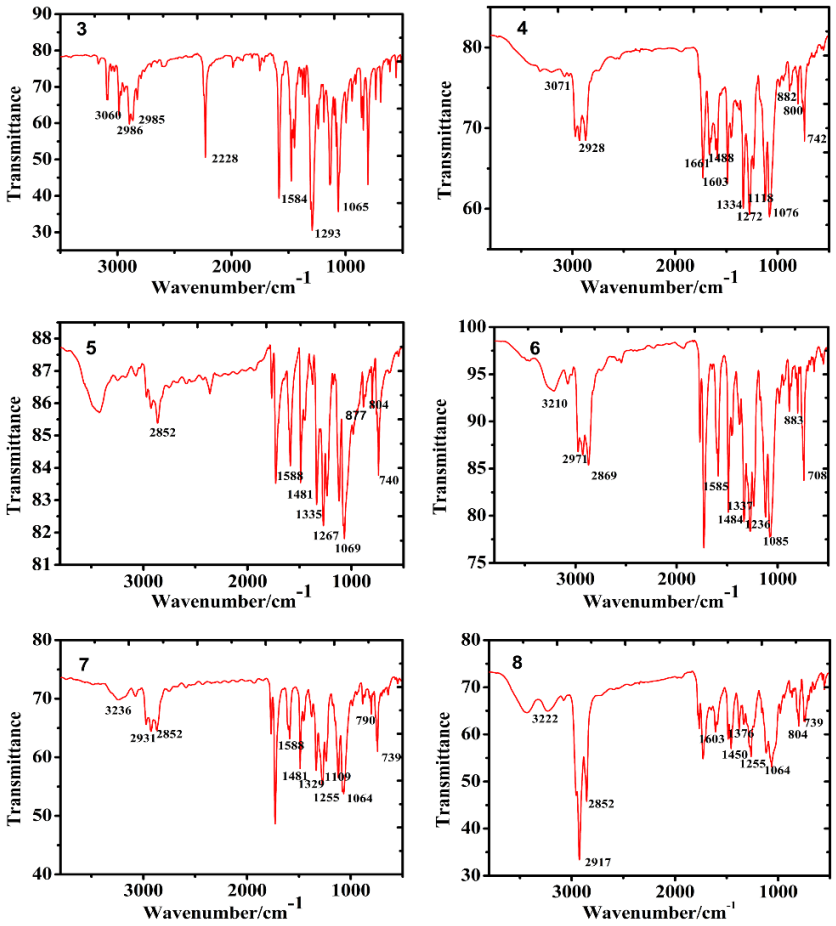

Fig. S13 FT-IR spectra of complexes phthalonitrile (**3**), (**InClPc**, **4**), (**(C_2)InPc**, **5**), (**(C_3)InPc**, **6**) (**(C_4)InPc**, **7**) and (**(C_5)InPc**, **8**).

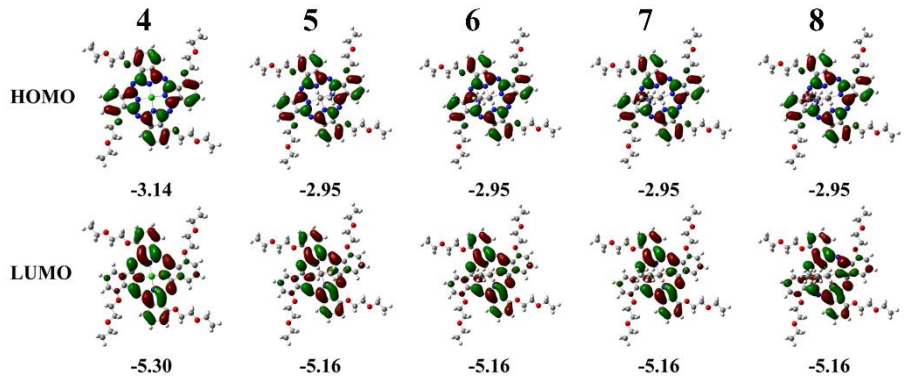

Fig. S14 Nodal patterns of the frontier π-MOs of 4, 5, 6, 7 and 8 in TD-DFT calculations.

Theoretical calculations were performed to study the HOMO/LUMO information of complexes **4-8** using the LANL2DZ with basis set of the 6-31G(d) level by the Gaussian 09 package. And PCM model with Dimethyl sulfoxide as the solvent were performed. Figure S14, shows the HOMO/LUMO gap energies of complexes **4-8**.

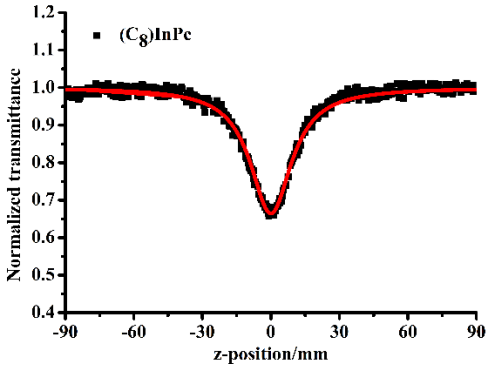

Fig. S15 Open-aperture Z-scan curve of the C_8 excited under 4ns pulses at 532 nm.

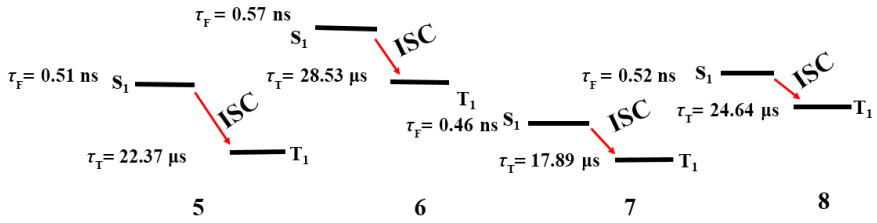

Fig. S16 Energy level diagrams to explain the dynamics of the transient state population of complexes **5-8**.

Table. S1 The values of the nonlinear absorption coefficients of phthalocyanine complexes studied at 532 nm using nanosecond pulses.

Sample	Wavelength	Concentration (mol L^{-1})	T (%)	Intensity (W/cm^2)	β/α_2 (cm/GW)	Reference
alkoxy phthalocyanines	532 nm, 6 ns	—	70	3.1×10^6	1650 (Pc1) 1850 (Pc2)	62
alkyl phthalocyanines	532 nm, 6 ns	5×10^{-4}	~75	6×10^6	310 (Pc1) 420 (Pc2)	63
InClPc	532 nm, 4 ns	2×10^{-4}	90	2.70×10^8	18.58	In this work
(C_2)InPc	532 nm, 4 ns	2×10^{-4}	88	2.70×10^8	22.15	In this work
(C_3)InPc	532 nm, 4 ns	2×10^{-4}	90	2.70×10^8	23.67	In this work
(C_4)InPc	532 nm, 4 ns	2×10^{-4}	90	2.70×10^8	24.45	In this work
(C_5)InPc	532 nm, 4 ns	2×10^{-4}	87	2.70×10^8	26.06	In this work