Supplemental Material

Tetra (C_{60}) lanthanum phthalocyanine: design, synthesis and investigation of third-order nonlinear optical properties.

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1. Characterisation of monomer 1

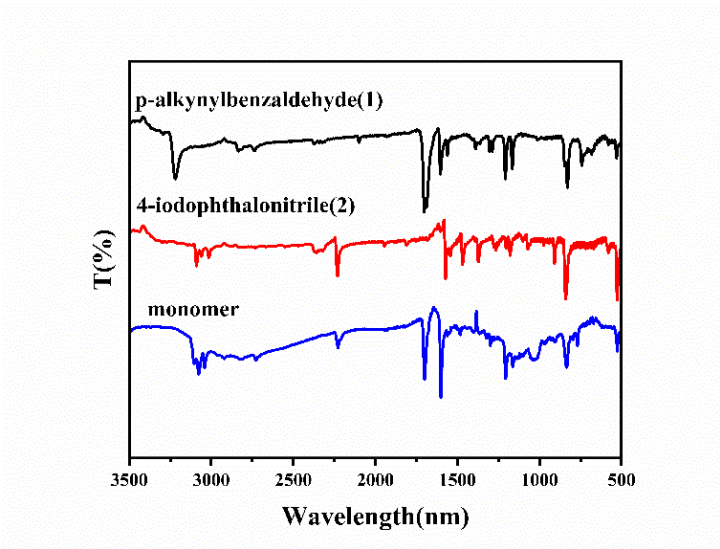

Fig. S1. FT-IR spectra of compounds (1), (2) and monomer.

The infrared spectra of (1), (2) and the monomer 1 are shown in Fig. S1. In the spectrum of the monomer 1, it can be seen that the vibrational absorption peak of CN is at 2230 cm^{-1}, and the stretching vibration absorption peak of C-H is near 1090 cm^{-1}; The peak around 660-900 cm^{-1} corresponds to the out-of-plane bending vibration of the phenyl C-C bond; and the peak at 1742 cm^{-1} corresponds to the stretching vibration of the C=O bond.

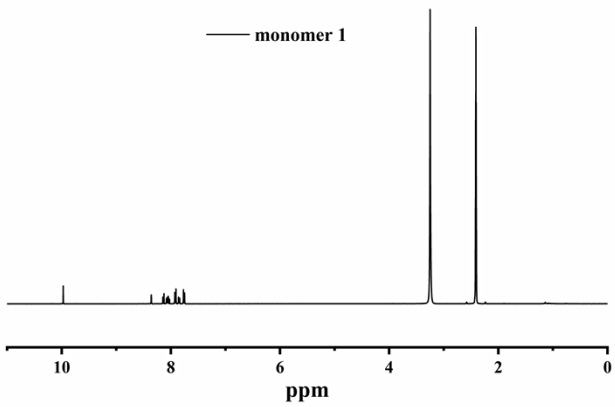

Fig. S2. ^{1}H NMR spectra of monomer 1.

The ^{1}H NMR spectra of monomer 1 is shown in Fig. S2. It exhibited the bands at approximately 7.85-8.49 ppm and 10.00 ppm, which were attributed to the H of Benzene and H of Aldehyde group. All the above results provide evidence of that monomer 1 has been successfully synthesized.

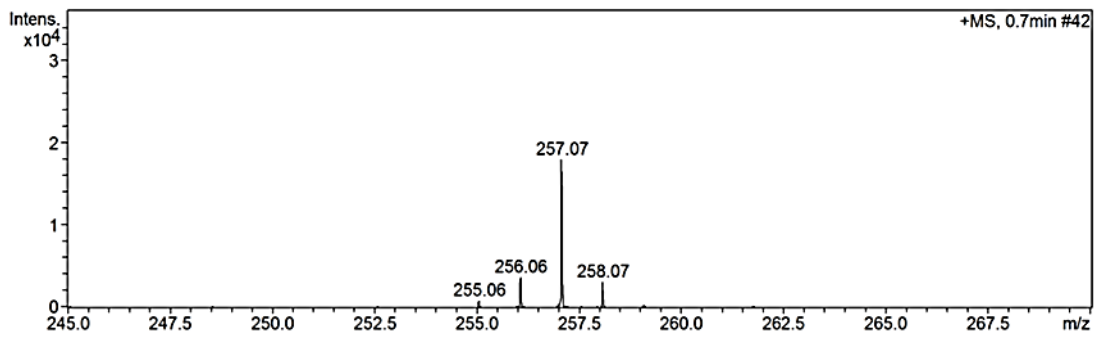

Fig S3. The high resolution mass spectrum of monomer 1

2. ^{1}H NMR spectra and MALDI-TOF-MS spectra of LaPc

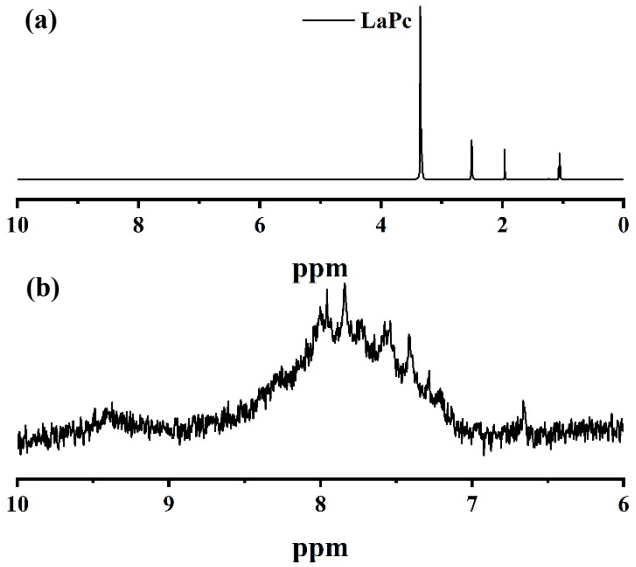

Fig. S4. (a) ^{1}H NMR spectra of LaPc; (b) the partial enlarged ^{1}H NMR spectra of LaPc.

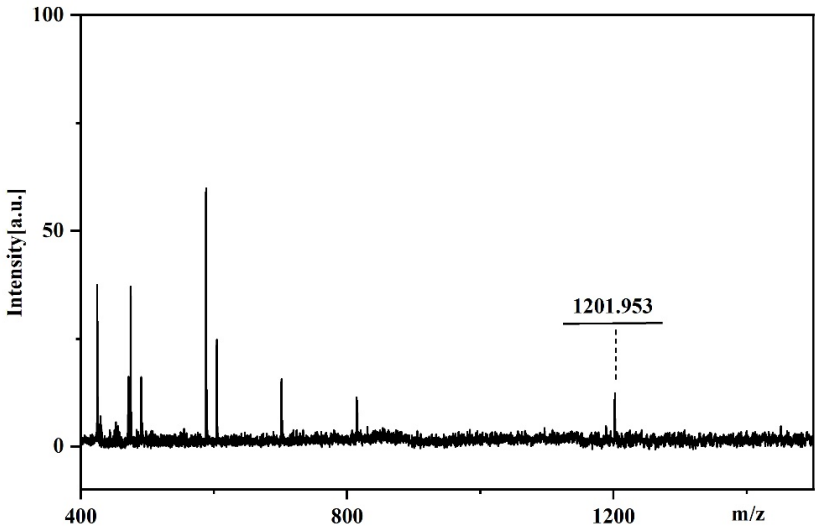

Fig S5. The MALDI-TOF-MS spectra of LaPc is shown in Fig S5.

3. ^{1}H NMR spectra and MALDI-TOF-MS spectra of tetra (C_{60})-LaPc

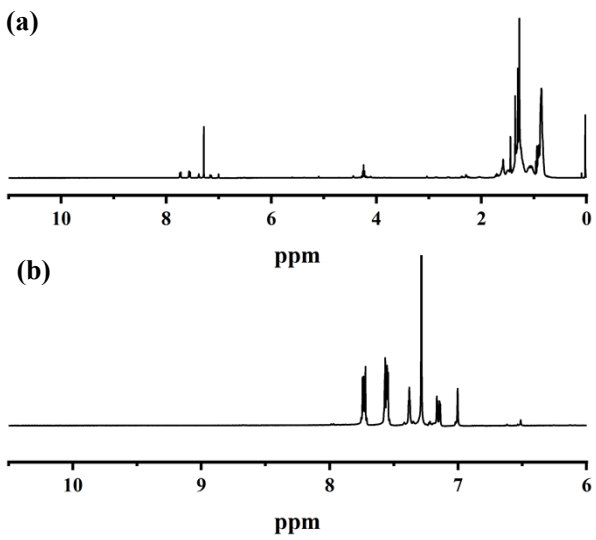

Fig S6. ^{1}H NMR spectra of tetra (C_{60})-LaPc with Chloroform-d ($CDCl_3$) as the solvent.

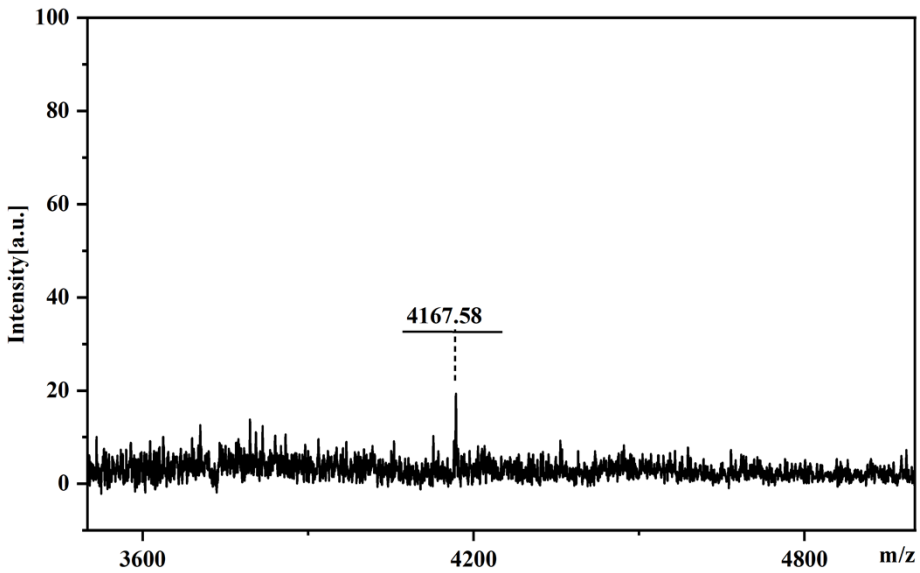

Fig S7. The MALDI-TOF-MS spectra of tetra (C_{60})-LaPc is shown in Fig S5.

4. XPS spectra

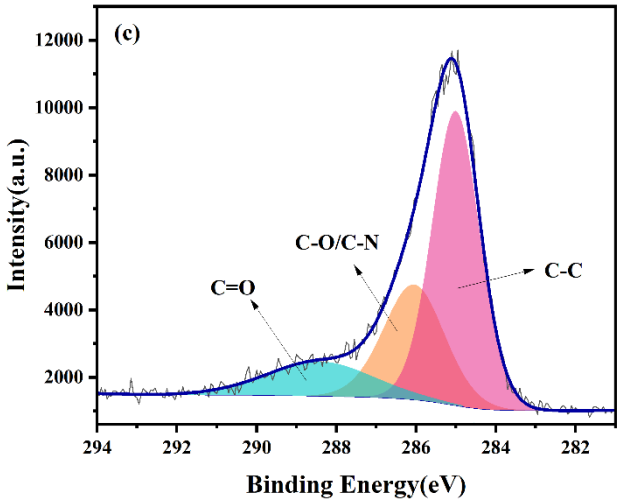

Fig. S8. XPS spectra of C 1s of LaPc.

5. Tauc spectra

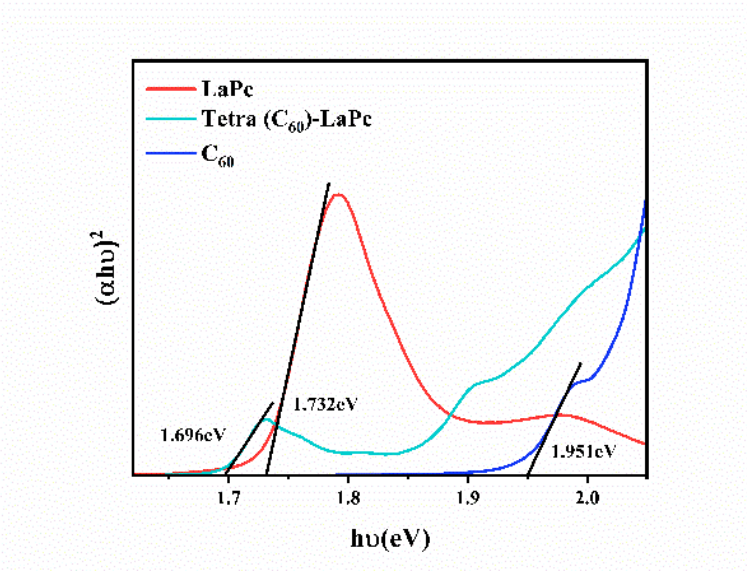

Fig. S9. Tauc spectra of C_{60}, LaPc and tetra (C_{60})-LaPc.

6. CV spectra

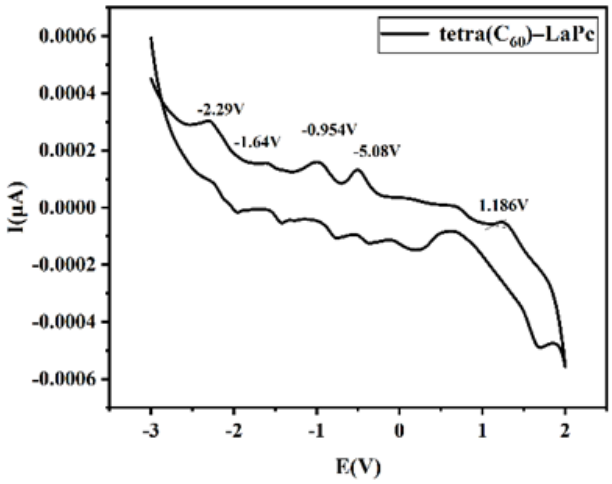

Fig S10. The CV spectra of tetra(C_{60})–LaPc.

Table S1. E_g, LUMO Energy Levels of the samples.

Samples	E_{LUMO} (eV)	E_g(eV)	λmax(1)	λmax(2)
LaPc	-3.275	1.732	693	705
C_{60}	-3.304	1.951	/	/
tetra(C_{60})–LaPc	-3.792	1.696	705	710

λmax (1) is the maximum absorption peak in the UV-Q band; λmax(2) is the maximum fluorescence emission peak.

7. UV–vis absorption and fluorescence emission spectra

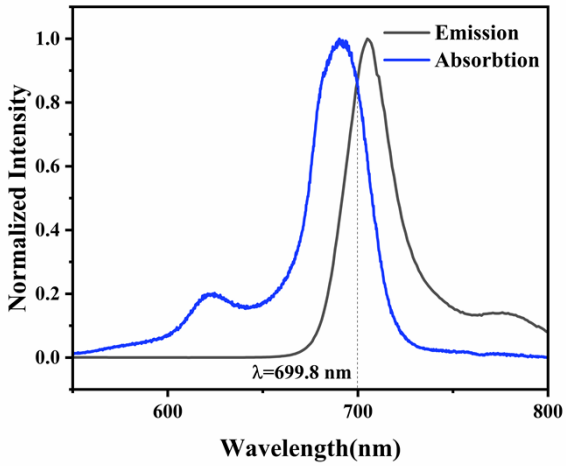

Fig. S11. The normalized curves (a) UV–vis absorption and fluorescence emission spectra.

8. Z-scan spectra

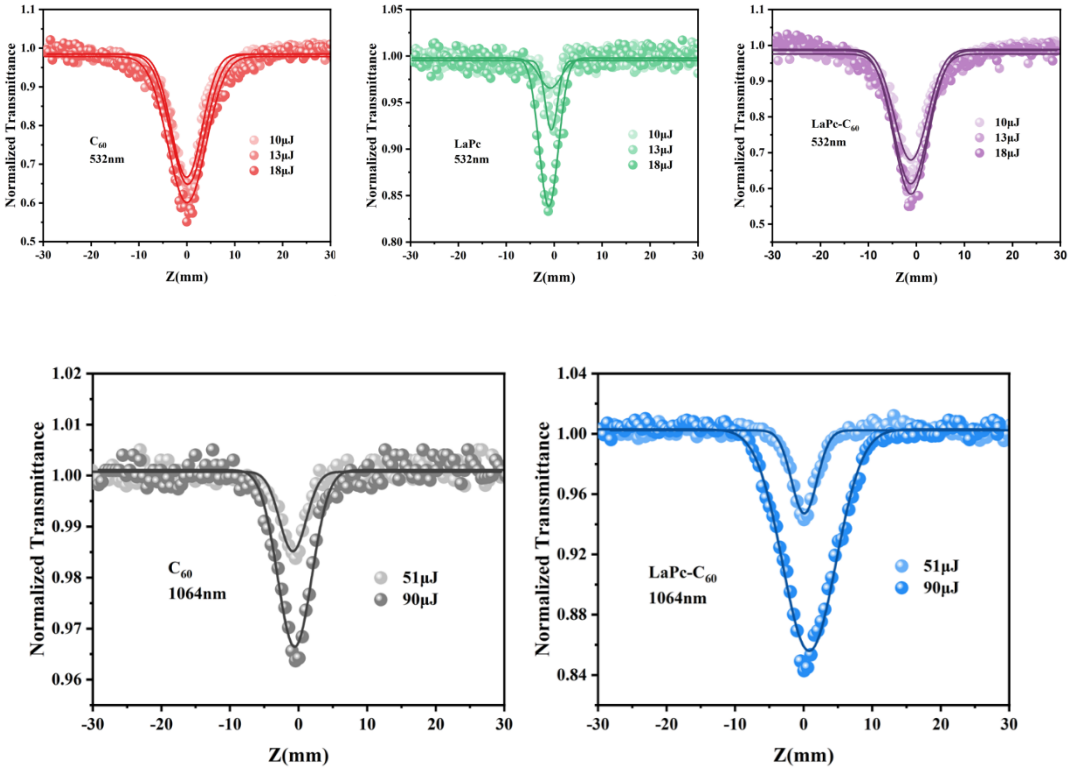

Fig S12. Open-aperture Z-scan curves of C_{60}, LaPc and tetra(C_{60})–LaPc nm excited by the different input energies at 532 nm and at 1064 nm with similar linear transmittance.

The changes in the curve of Z-scan at different incident light intensities have been shown in Fig. S11. The third-order non-linear optical intensities of C_{60}, LaPc and tetra(C_{60})–LaPc increase with the growing incident laser intensity, and in particular the anti- saturation absorption of tetra(C_{60})–LaPc is significantly enhanced, which can be attributed to its effective intramolecular PET/ET process.