Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Click chemistry functionalization improving the wideband optical-limiting performance of fullerene derivatives

Supporting Information

Contents:

1. UV-vis property

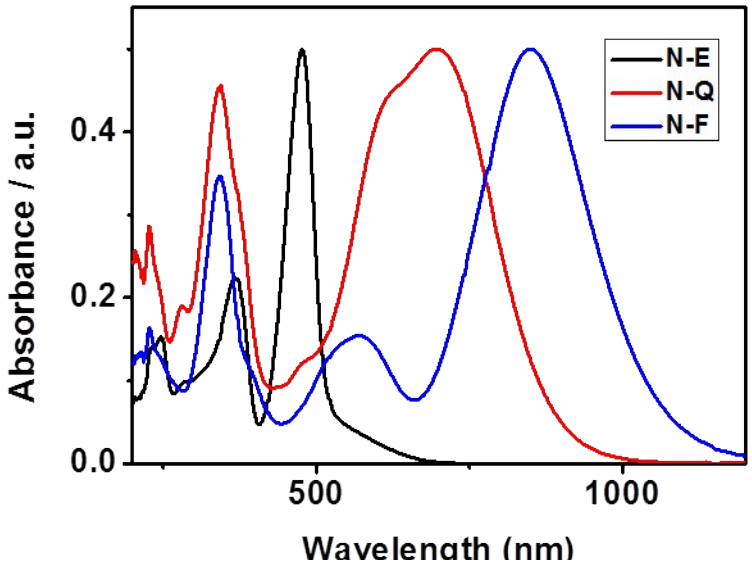


Fig. S1. UV-vis spectra of the compounds **(N-E, N-Q** and **N-F)** in dichloromethane at rt.

2. Electrochemical Test

The redox properties of all the novel compounds were investigated by cyclic voltammetry (CV) in dichloromethane (1×10^{-3} M, 0.1 M nBu$_4$NPF$_6$, all potentials vs. the ferricinium/ferrocene couple (Fc^+/Fc)). The energy levels were calculated using the Ferrocene (Fc) value of -4.8 eV with respect to the vacuum level, which was defined as zero. The measured oxidation potential of Fc (vs Ag/AgCl) was 0.18 V. Therefore, the HOMO energy (E_{HOMO}) levels of the products could be calculated by the equation $E_{HOMO} = -e[E_{onset}(ox) - E_{1/2,Fc} + 4.8\ V]$ and the LUMO energy (E_{LUMO}) levels could be estimated by the equation $E_{LUMO} = -e[E_{onset}(red) - E_{1/2,Fc} + 4.8\ V]$, where $E_{1/2,Fc}$ standards for the half-wave potential of Fc/Fc^+.

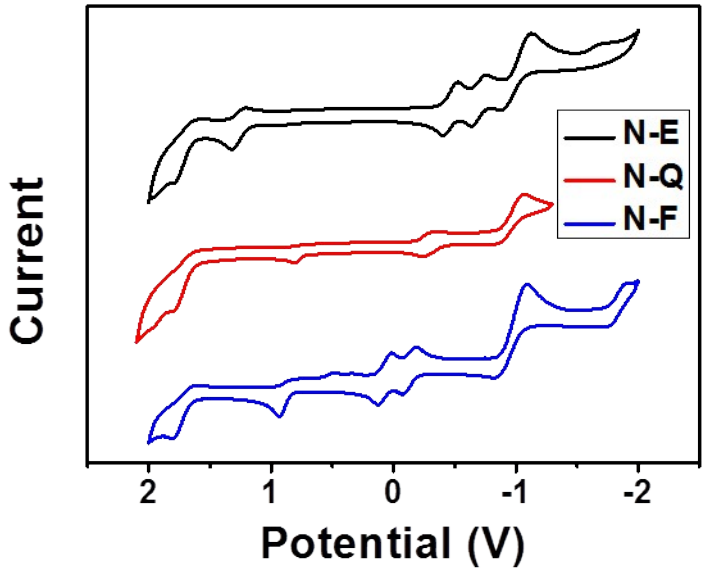


Fig. S2. Cycle voltammograms of the compounds **(N-E, N-Q** and **N-F)** in dichloromethane /Bu$_4$NPF$_6$ at rt.

3. DFT simulation

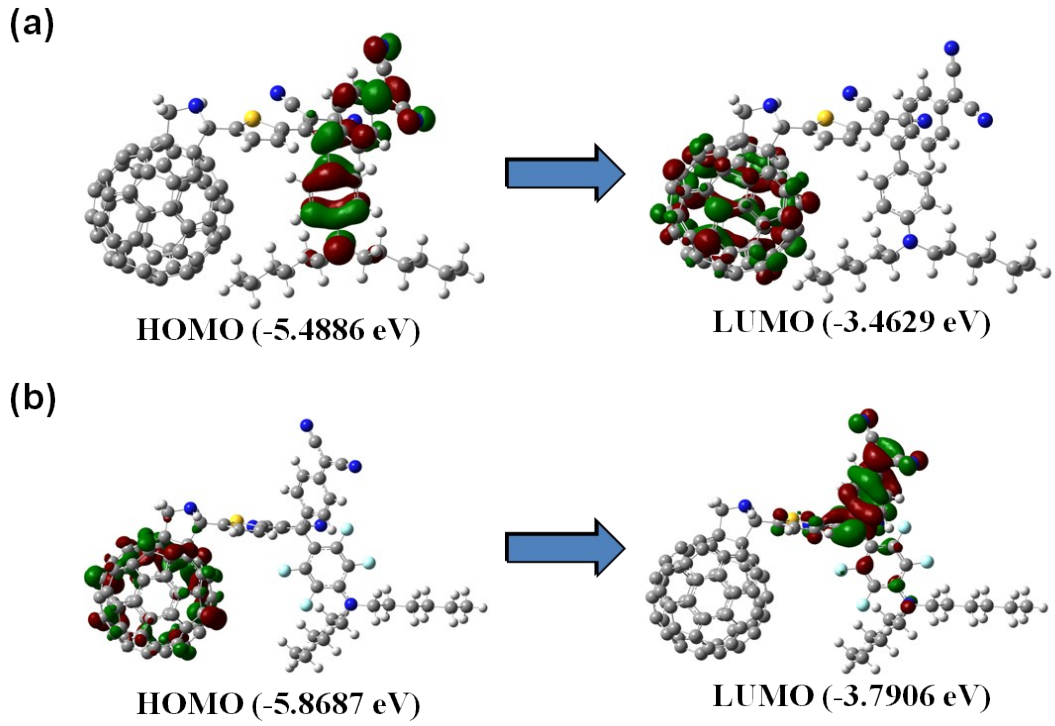


Fig. S3. The optimized structures and electron distributions of HOMO and LUMO levels of N-Q-C60 (a) and N-F-C60 (b) models

4. Measurement of third-order nonlinear optical and parameters calculation

4.1 Measurement

The nonlinear optical properties (NLO) response was measured by means of Z-scan technique, employing 21 ps laser pulses at 532 nm and 1064 nm delivered by a mode-locked Nd:YAG laser. Z-scan is a relatively simple experimental technique allowing for the simultaneous determination of the real and imaginary parts of the third-order susceptibility $\chi^{(3)}$.[2] All of the samples were measured at 10^{-6} M solution in dichloromethane solvent (specpure). The solvent itself does not show any third-order nonlinearity under our experimental conditions. The nonlinear refractive index n_2 and the nonlinear absorption coefficient β would be available under measurement. The real and imaginary parts of the third-order nonlinear susceptibility $\chi_{Re}^{(3)}$ and $\chi_{Im}^{(3)}$ and

the third-order nonlinear susceptibility $\chi^{(3)}$ can be calculated by the previous method given in **4.2** (as followed).

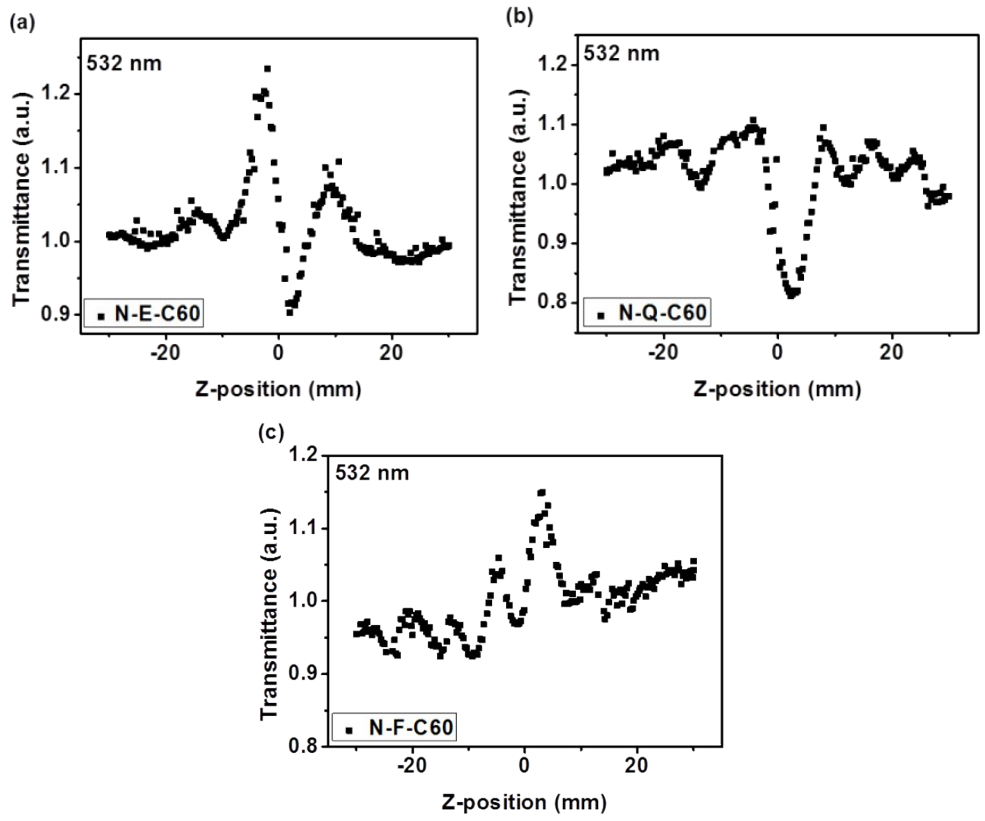
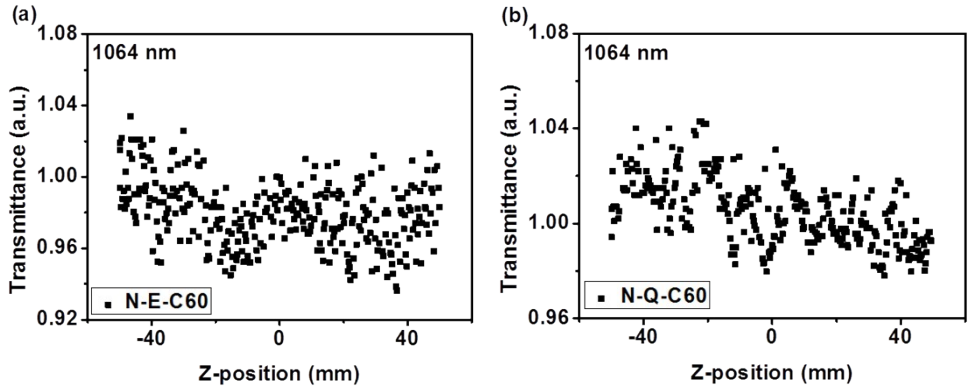


Fig. S4. Z-scan curves in dichloromethane at 532 nm: (a) Close aperture trace for **N-E-C60**; (b) Close aperture trace for **N-Q-C60**; (c) Close aperture trace for **N-F-C60**.



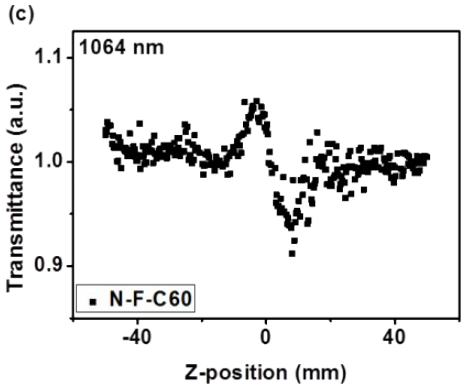


Fig. S5. Z-scan curves in dichloromethane at 1064 nm: (a) Close aperture trace for **N-E-C60**; (b) Close aperture trace for **N-Q-C60**; (c) Close aperture trace for **N-F-C60**.

4.2 Calculation

In theory [1-3], the normalized transmittance for the open aperture can be written as:

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}} \quad \text{for } |q_0| < 1 \qquad (1)$$

where $q_0(z) = \frac{\alpha I(t) L_{eff}}{1 + Z^2/Z_0^2}$, α is the nonlinear absorption coefficient, $I_0(t)$ is the intensity of laser beam at focus (z =0), $L_{\text{eff}} = |1 - \exp(-\alpha_0 L)|/\alpha_0$ is the effective thickness with α_0 the linear absorption coefficient and L the sample thickness, z_0 is the diffraction length of the beam, and z is the sample position. Thus, the nonlinear absorption coefficients of the compounds can be determined by fitting the experimental data using Eq. (1).

The normalized transmission for the closed aperture Z-scan is given by the following:

$$T = 1 + \frac{4\Delta\Phi_0 x}{(x^2+9)(x^2+1)} \qquad (2)$$

where x =z/z_0 and $\Delta\Phi$ is on-axis phase change caused by the nonlinear refractive index of the sample and $\Delta\Phi = 2\pi n_2 I_0 L_{eff}/\lambda$. Thus, the nonlinear refractive coefficients of the compounds can be determined by fitting the experimental data using Eq.(2).

The $\chi^{(3)}$ can be calculated by Eq.(3):

$$|\chi(3)| = \sqrt{\left|\frac{n_0^2 c}{120\pi^2} n_2\right|^2 + \left|\frac{c^2 n_0^2}{240\pi^2 \omega}\beta\right|^2} \quad (3)$$

where $\omega = 2\pi c/\lambda$, c is the speed of light, n_0 is the refractive e index of the medium.

References:

[1] Sheik-Bahae M, Said AA, Wei TH, Hagan DJ, Vanstryland EW. Sensitive measurement of optical nonlinearities using a single beam. IEEE J Quantum Electron 1990; 26:760-769.

[2] Wang X, Guang SY, Xu HY, Su XY, Yang JY, Song YL, Lin NB, Liu XY. Thermally stable oxadiazole-containing polyacetylenes: Relationship between molecular structure and nonlinear optical properties. J Mater Chem 2008; 18: 4204-4209.

[3] Zhang WS, Wang D, Cao H, Yang H. Energy-level tunable click functionalization of [60]fullerene for nonlinear optics. Tetrahedron 2014; 21: 573-577.