Supporting Information

Note S1. Stokes shift fitting method.

The stokes shift of QTPA1 and QTPA2 as a function of polarity of solvent is given in Figure 1(C), which is fitted by linear function of

$$\Delta \bar{v}\left(\bar{v}_{abs} - \bar{v}_{em}\right) = \frac{2\Delta\mu^2 \Delta f}{hca^3} + const$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

where ε and n are the dielectric constant and the refractive index of the solvents, respectively; v_a (v_f) is the wavenumber (cm^{-1}) of the absorption (emission) maximum, h (6.6×10^{-34} J·s) is the Planck constant, c (3.00×10^8 m·s^{-1}) is the light velocity, ε_0 (8.85×10^{-12} C·V^{-1}·m^{-1}) is the vacuum permittivity and $\Delta\mu$ ($=\mu_e - \mu_g$) is the dipole moment difference of the solute between S_0 and S_1 state.

Note S2. Calculation Details of nonlinear absorption coefficient (β) and the two-photon absorption cross section (σ).

The influence of the solvent nonlinearity could be excluded. The two-photon absorption (TPA) coefficient β of TOND in three solvents can be obtained by fitting the experimental results with equation:

$$T(z, S = 1) = \sum_{m=0}^{\infty} \frac{(-q_0(z,0))^m}{(m+1)^{3/2}}$$

where $q_0(z) = \beta I_0 / (1 + \frac{z^2}{z_0^2})$; $z_0 = k\omega^2/2$ is the Rayleigh length, $k = 2\pi/\lambda$ is the wave vector; ω_0 is beam waist radius of Gaussian pulse, and I_0 is the pulse irradiance.

The TPA coefficient β is related to the TPA cross section σ by using

$$\sigma = \frac{\beta h v 10^3}{Nc}$$

where N is Avogadro's number, c is the concentration, h is Planck's constant, and v is the laser frequency. In this experiment, the concentration of QTPA is 5×10^{-4} M. σ is expressed in Göppert-Mayer units (GM), with 1 GM = 1×10^{-50} cm^4 s molecule^{-1}

photon^{-1}.

Note S3. Calculation Details of Temperature-Dependent PL Quantum Yield.

The PL quantum yield can be defined as the ratio of the number of emitted photons to the number of absorbed photons by a luminescent material:

$$PLQY = \frac{N_{em}}{N_{abs}}$$

The most straightforward method for the determination of PLQY values presents the absolute measurement of N_{abs} and N_{em} with an integrating sphere setup. The PLQY of QTPA1 and QTPA2 film at room temperature can be described by:

$$PLQY = \frac{\int \frac{\lambda}{hc}(I^{sample}_{em}(\lambda) - I_{em}(\lambda))d\lambda}{\int \frac{\lambda}{hc}(I_{ex}(\lambda) - I^{sample}_{ex}(\lambda))d\lambda}$$

and λ is the wavelength; h is Planck's constant; c is the velocity of light; I^{sample}_{ex} and I_{ex} are the integrated intensities of the excitation light with and without a sample, respectively.

After obtaining the temperature-dependent absorption and PL spectra of the sample, the quantum yield at different temperatures QY_2 can be obtained from QY_1. The general equation used in the determination of relative quantum yields is given in

$$\frac{QY_2}{QY_1} = \frac{I_{em2}}{I_{em1}} \times \frac{A_1}{A_2} \times \frac{\lambda_{ex1}}{\lambda_{ex2}} \times \frac{\eta_2}{\eta_1}$$

Among them, I_{em} is the integrated area under the corrected emission spectrum; A is absorbance at the excitation wavelength; λ_{ex} is the excitation wavelength; η is the collection efficiency of the system. In our experiments, the system and test conditions are unchanged, which means that $\eta_2 / \eta_1 \approx 1$, and the excitation wavelength remains the same.

Note S4. Calculation Details of the Radiative Lifetime.

The PL decay can be described by:

$$I_{PL}(t) = \sum_{i=1}^{n} k_i exp(-t/\tau_X^i)$$

,

where τ_X^i is the effective single-exciton lifetime given by

$$\tau_X^i = \tau_{r,X}\tau_{nr,X}^i/(\tau_{r,X} + \tau_{nr,X}^i),$$

and k_i is the relative fraction of the QDs in the i-th sub-ensemble;the k_i coefficients are

normalized such as $\sum_{i=1}^{n} k_i = 1$ .The PL quantum yield(QY)of the individual sub-ensemble is given by:

$$q_i = \tau_X^i/\tau_{r,X},$$

And the total PL QY of the entire QD sample(Q) can be expressed as:

$$Q = \sum_{i=1}^{n} k_i q_i = \tau_{r,X}^{-1}\sum_{i=1}^{n} k_i \tau_X^i,$$

This lead to the following expression for the radiative lifetime:

$$\tau_{r,X} = Q^{-1}\sum_{i=1}^{n} k_i \tau_X^i = Q^{-1}\langle\tau_X\rangle,$$

Where $\langle\tau_X\rangle$,is the average exciton lifetime in the QD ensemble expressed as:

$$\langle\tau_X\rangle = \sum_{i=1}^{n} k_i \tau_X^i$$

	QTPA1		QTPA2	
	abs (nm)	PL (nm)	abs (nm)	PL (nm)
CHX	413	484	414	483
TOL	422	508	422	506
o-dichlorobenzene	425	541	425	555
DCM	429	555	430	566
THF	430	573	431	586
TCM	431	581	432	607
EToH	432	609	433	617
ACE	433	623	434	623
DMF	435	631	436	642
DMSO	438	643	438	658

Table S1. The relevant data of solution absorption and photoluminescence emission spectra of QTPA1 and QTPA2.
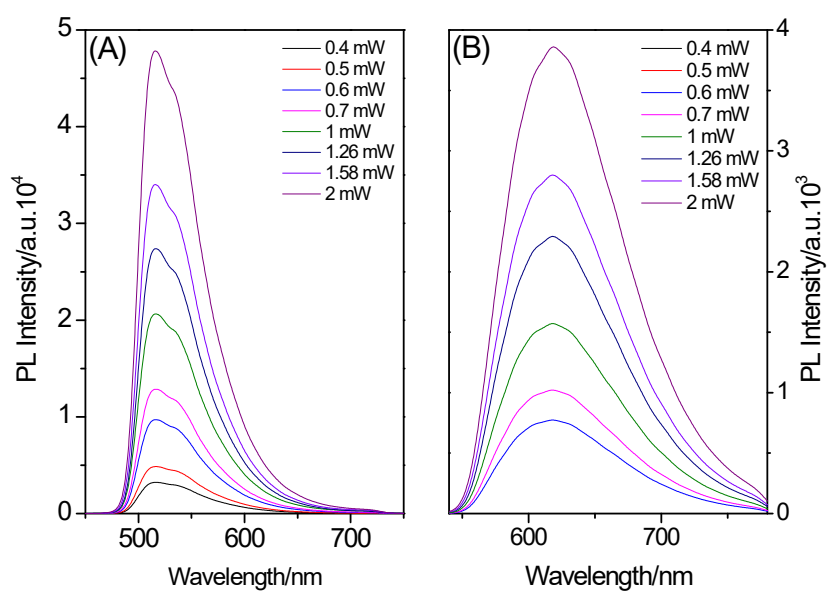
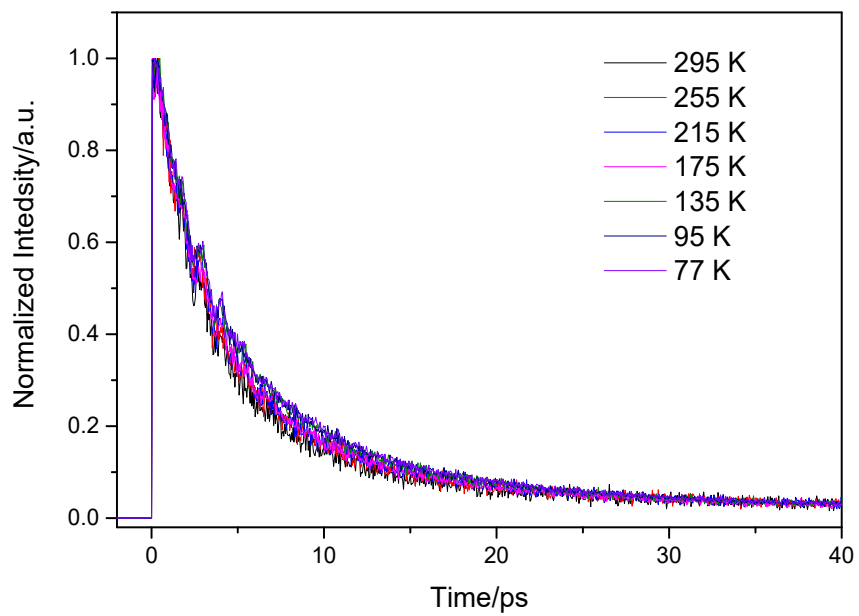Figure S1. Two-photon fluorescence (TPF) spectra of QTPA1 in TOL (A) and DMF (B).

Figure S2. Temperature-dependent fluorescence lifetime of QTPA2.