Supporting Information

Table S1. The crystal data collection and the refinement parameters of T-1 and T-3

	T-1	T-3
Empirical formula	C H1.73 N O0.03	C36 H32 F6 N3 P
Formula weight	28.2	651.62
Temperature	296(2)K	298(2)K
Wavelength	0.71073Å	0.71069 Å
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$
a/Å	9.61(13)	10.37(5)
b/Å	9.26(13)	14.01(5)
c/Å	55.98(8)	24.32(5)
Volume	4975(12) $Å^3$	3257(2) $Å^3$
Z, Calculated density	146, 1.374 Mg/m^3	4, 1.329 Mg/m^3
Absorption coefficient	0.097 mm^{-1}	0.149 mm^{-1}

F(000)	2182	1352
Crystal size	0.30 ×0.20 × 0.10 mm	0.30 ×0.20 × 0.10 mm
Theta range for date collection	1.46 to 25.00 deg.	1.66 to 25.00 deg.
Limiting indices	-11<=h<=11, -10<=k<=10, -66<=l<=66	-12<=h<=11, 16<=k<=16, -28<=l<=27
Reflections collected/unique	29779 / 8315 [R(int) = 0.0780]	23007 / 11327 [R(int) = 0.0253]
Completeness to theta=25.00	95.1 %	98.6 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission		0.9853 and 0.9567
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8315 / 155 / 655	11327 / 0 / 940
Final R indices [I>2sigma(I)]	R1 = 0.1147, wR2 = 0.3099	R1 = 0.0953, wR2 = 0.2858
R indices (all data)	R1 = 0.1814, wR2 = 0.3488	R1 = 0.1442, wR2 = 0.3257

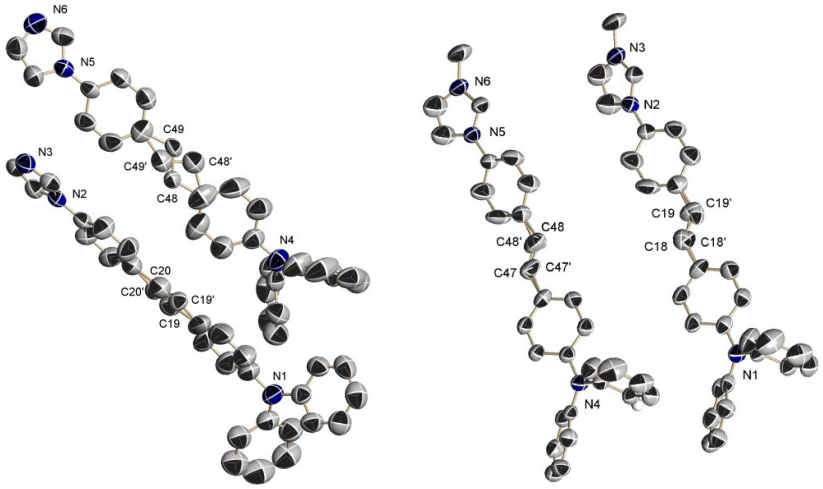

Figure S1. The crystal structures of T-1(left) and T-3(right). H atoms, anions and solvents molecules have been omitted for clarity

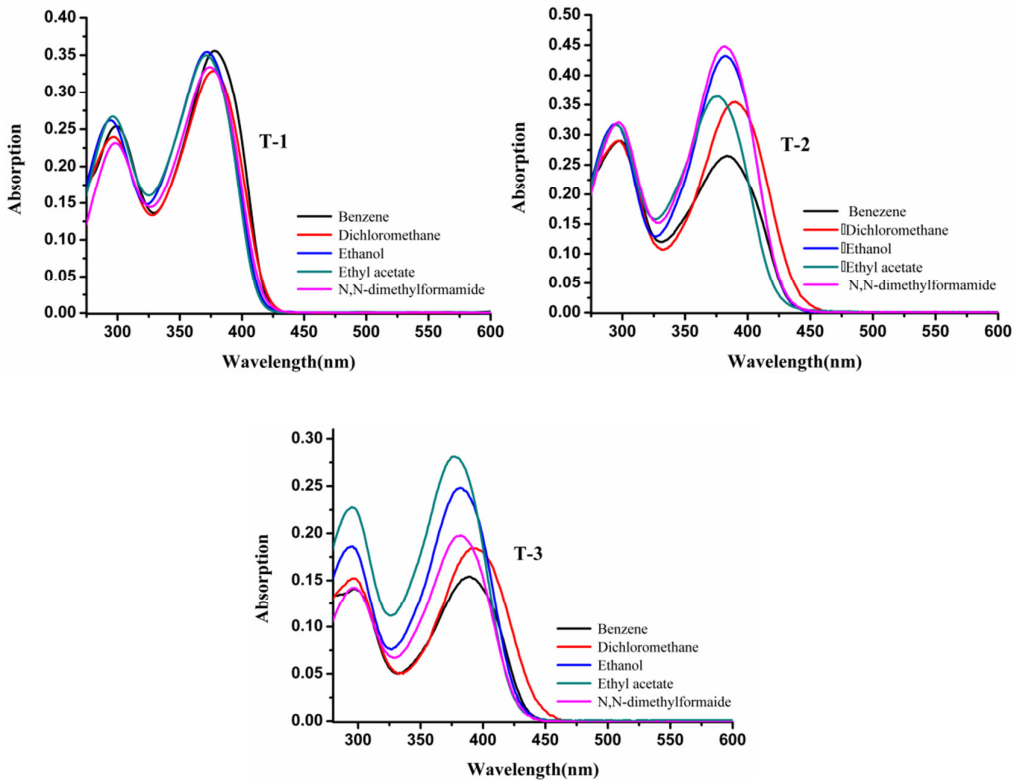

Figure S2. UV-vis spectra of **T-1, T-2** and **T-3** (1×10^{-5} M) in different solvents

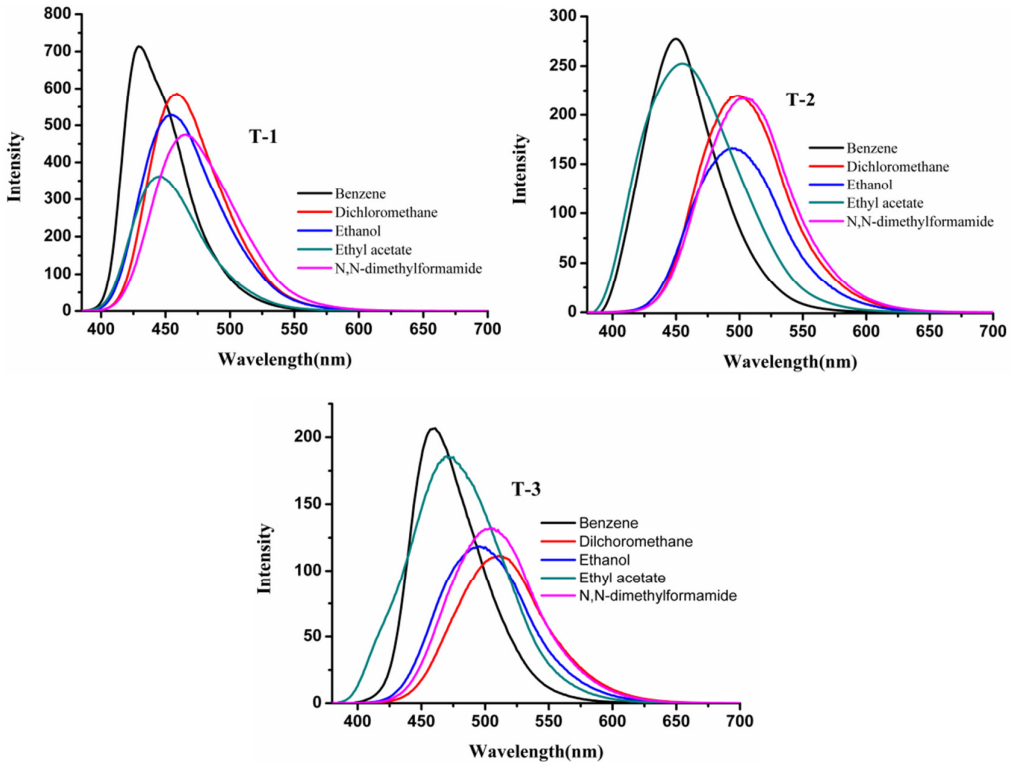

Figure S3. Single-photon fluorescence spectra of **T-1, T-2** and **T-3** (1.0×10^{-5}M) in different solvents

Fluorescence quantum yield

The fluorescence quantum yields (Φ) were determined by using Rhodamine-B as the reference according to the literature method [1]. Quantum yields is corrected as follows:

$$\Phi_s = \Phi_r \frac{A_r \eta_s^2 D_s}{A_s \eta_r^2 D_r}$$

where the *s* and *r* indices designate the sample and reference samples, respectively, *A* is the absorbance at λ_{exc}, η is the average refractive index of the appropriate solution, and *D* is the integrated area under the corrected emission spectrum[2] .

The Lippert-Mataga equation

The Lippert-Mataga equation is as follow:

$$\Delta\nu = \frac{2\Delta f}{4\pi\varepsilon_0 \hbar c a^3}(\mu_e - \mu_g)^2 + b$$

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

in which $\Delta\nu = \nu_{abs} - \nu_{em}$ stands for Stokes shift, ν_{abs} and ν_{em} are absorption and emission frequency (cm^{-1}), $\hbar$ is the Planc's constant, c is the velocity of light in vacuum, a is the Onsager radius and b is a constant. Δf is the orientation polarizability, ε is the refractive index, n is the dielectric constant, μ_e and μ_g are the dipole moments of the emissive and ground states, respectively and ε_0 is the permittivity of the vacuum. $(\mu_e-\mu_g)^2$ is proportional to the slope of the Lippert-Mataga plot.

Two photon absorption cross section (δ)

2PA cross sections (δ) of samples is determined by Eq.:

$$\delta = \delta_{ref} \frac{\Phi_{ref}}{\Phi} \frac{c_{ref}}{c} \frac{n_{ref}}{n} \frac{F}{F_{ref}}$$

Where the '*ref*' subscript represents the reference molecule (here fluorescein in aqueous solution of sodium hydroxide (pH = 11) at a concentration of 1.0×10^{-3} mol L^{-1} was used as the reference). δ is the TPA cross-sectional value, c is the concentration of the solution, n is the refractive index of the solution, F is the 2PEF integral intensities of the solution emitted at the exciting wavelength, and Φ is the fluorescence quantum yield. The δ_{ref} value of reference was taken from the literature[3].

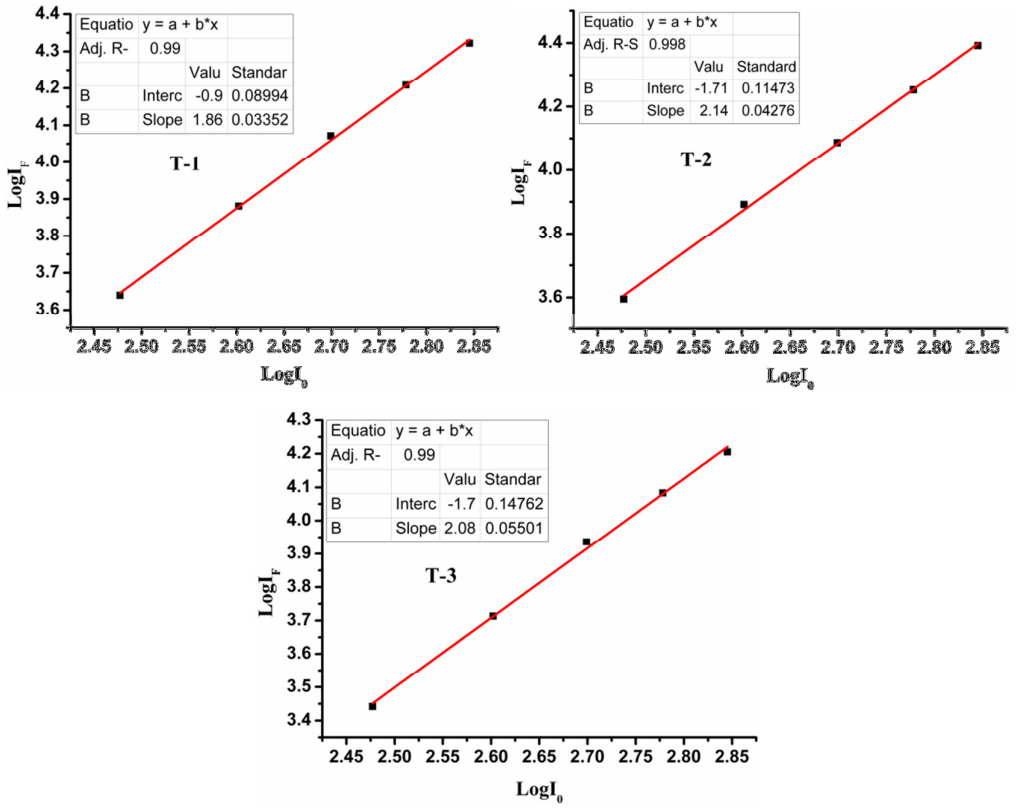

Figure S4. Output fluorescence (I_0) vs. the square of input laser power $(I_F)^2$ at 760nm for **T-1, T-2** and **T-3** in DMF

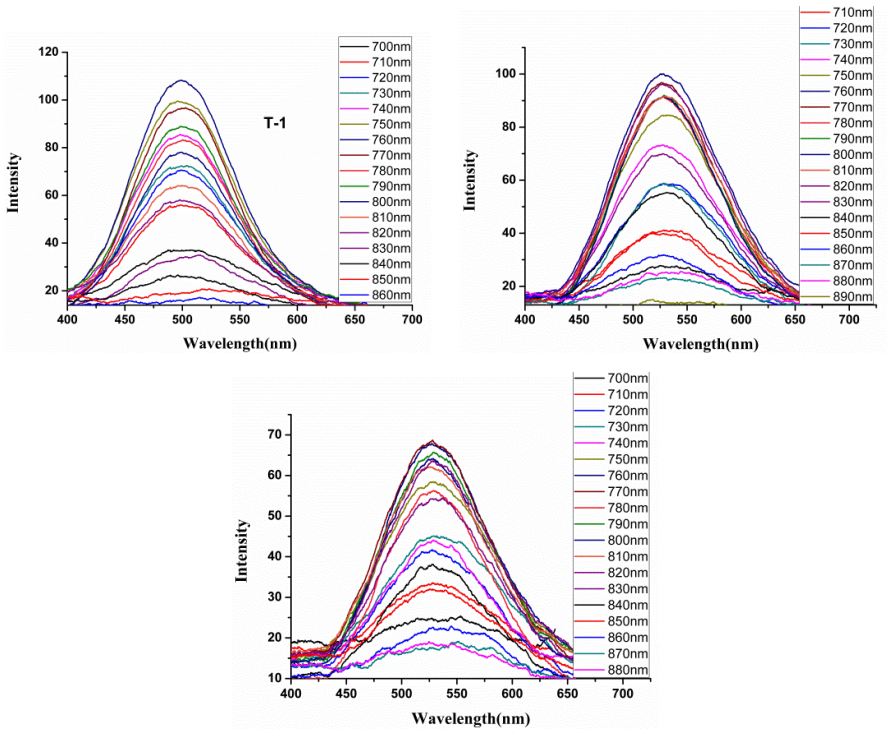

Figure S5. Two-photon exited fluorescence (TPEF) of **T-1**, **T-2**, and **T-3** in DMF

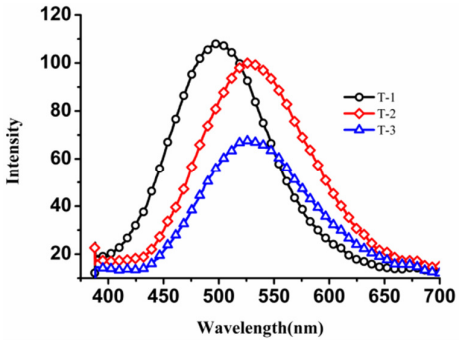

Figure S6. the two-photon excited fluorescence spectra of **T-1**, **T-2** and **T-3** (excitation wavelength at 760 nm, energy of 500 mW, c = 1.0×10^{-3} molL-1) in DMF

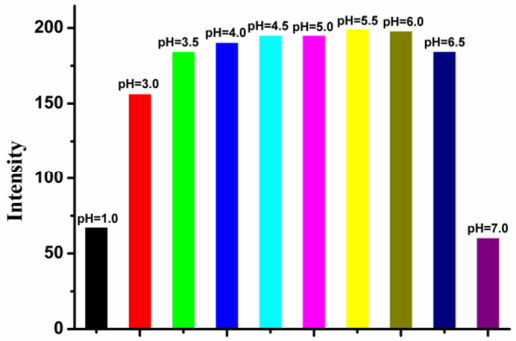

Figure S7. Single-photon fluorescence spectra of **T-1** (1.0×10^{-5}M) with different pHs in water

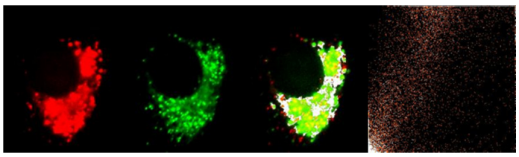

Figure S8. T-1 co-localizes to lysosomes in live HepG2 cells

Reference

[1] a. Kubin RF, Fletcher AN. Fluorescence quantum yields of some rhodamine dyes[J]. Journal of Luminescence, 1983; 27(4): 455-462. b. Karstens T, Kobs K. Rhodamine B and

rhodamine 101 as reference substances for fluorescence quantum yield measurements. The Journal of Physical Chemistry, 1980; 84(14): 1871-1872.

[2] Gray TG, Rudzinski CM, Meyer EE, Holm R, Nocera DG. Spectroscopic and photophysical properties of hexanuclear rhenium (III) chalcogenide clusters. Journal of the American Chemical Society. 2003;125(16):4755-70.

[3] He GS, Tan LS, Zheng Q, Prasad, P. N. Multiphoton absorbing materials: molecular designs, characterizations, and applications. *Chemical reviews*, 2008; *108*(4): 1245-1330.