Supporting Information

Turning on a high-rate-capability fluorescence resonance energy transfer in quantum dots-molecule system via high pressure

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Table S1 Rh640 Absorption (Abs) Peak Position and Spectral Overlap J(λ) of the Rh640 dye Abs and QD photoluminescence (PL) at different pressures.

Pressure (GPa)	Rh640 Abs Peak Position (nm)	Spectral Overlap J(λ) (1×10^9cm^{-1}nm^4M^{-1})
1 atm	574	0
0.3	574	0.380
0.7	575	0.436
0.9	576	0.836
1.2	576	1.847
1.8	567	3.909
2.1	568	4.979
2.6	569	11.13
3.3	569	13.00
3.6	580	13.96

The spectral overlap $J(\lambda)$ are calculated by the equation: $J(\lambda)= \int_0^{\infty} F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$ is a quantitative measure of the donor–acceptor spectral overlap over all wavelengths, where F_D and ε_A represent the donor PL (normalized dimensionless spectrum) and acceptor absorption extinction coefficient spectrum, respectively[1].
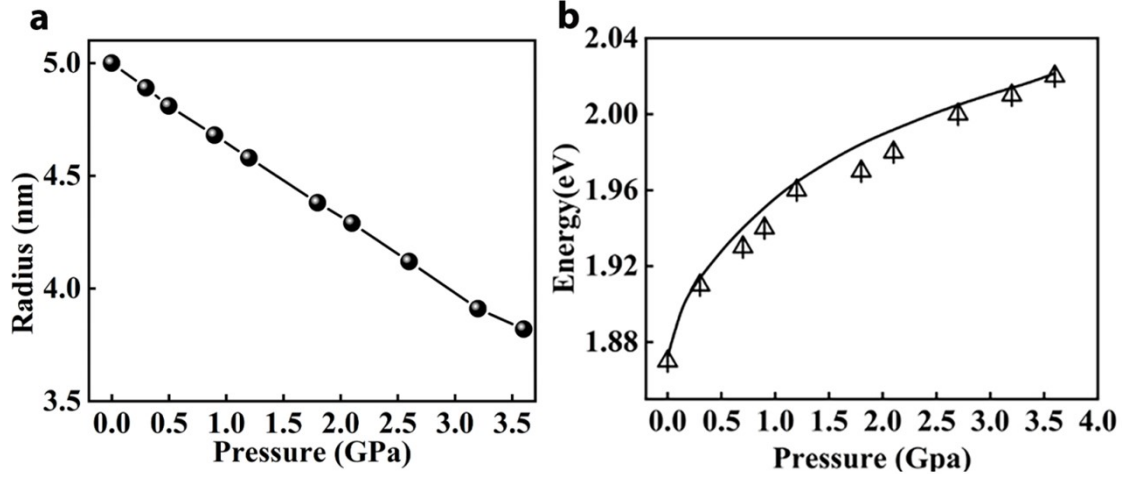
Fig. S1 (a) The QD radius dependence with pressure from atmospheric pressure to 3.6GPa. (b) The QD band gap with pressure from atmospheric pressure to 3.6GPa. The solid lines correspond to the linear fittings.

The dependence of QD band gap with radius $E(R)$ can be described by the following expression[2]:

$$E(R) = Eg + \frac{\hbar^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)\frac{\pi^2}{R^2} - 1.786\frac{e^2}{\epsilon_2 R} + \frac{e^2}{R}\sum_{n=1}^{\infty}\overline{a_n}\left(\frac{S}{R}\right)^{2n} \tag{1}$$

With $a_n = \left[(\epsilon - 1)(n + 1)/\epsilon_2(\epsilon n + n + 1)\right]$. Eg is the bulk band gap, and R is the radius of the QD. Obviously, each of the terms in eq 1 closely depends on the nanoparticle radius. Further, the change of the QD radius induced by pressure can be described by the Murnaghan's equation[3]:

$$D = \frac{D_0}{\left[(PB'/B) + 1\right]^{1/3B'}} \tag{2}$$

where P is the pressure, B the bulk modulus, and B' its pressure derivation. D_0 is the QD diameter at atmospheric pressure.
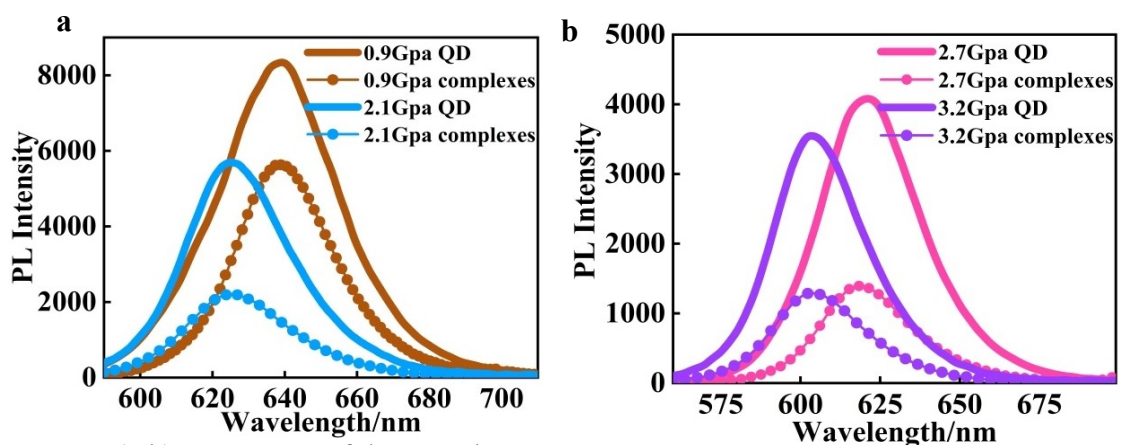
Fig. S2 (a,b) PL spectra of the QD alone and QD-Rh640 complexes with pressure from 0.9 to 3.2 GPa.

a 0.7Gpa

b 1.2Gpa

c 1.8Gpa

g 0.7Gpa

h 1.2Gpa

i 1.8Gpa
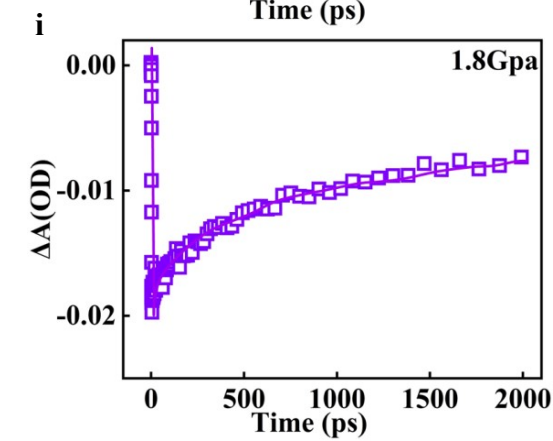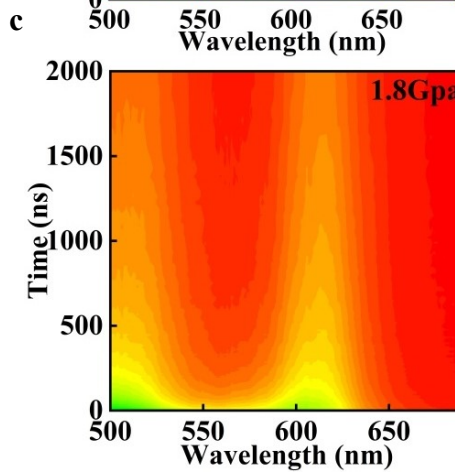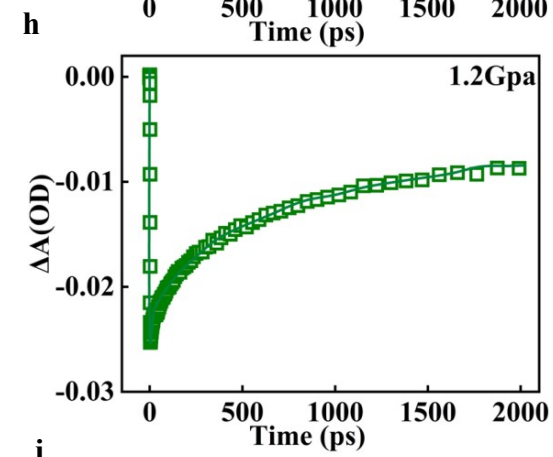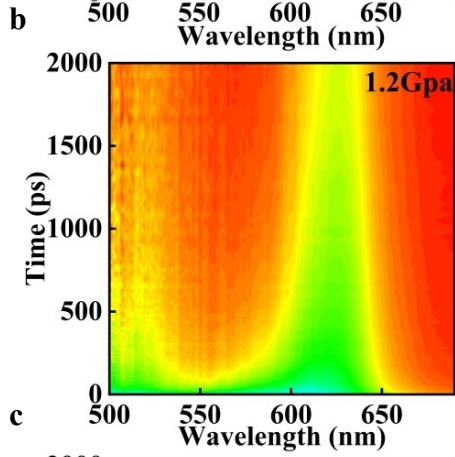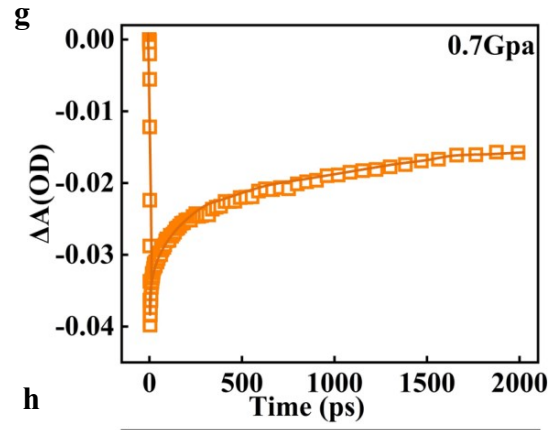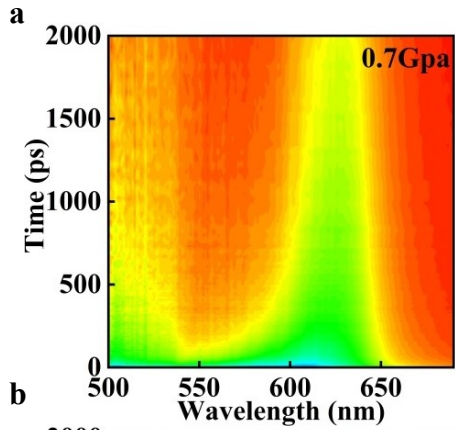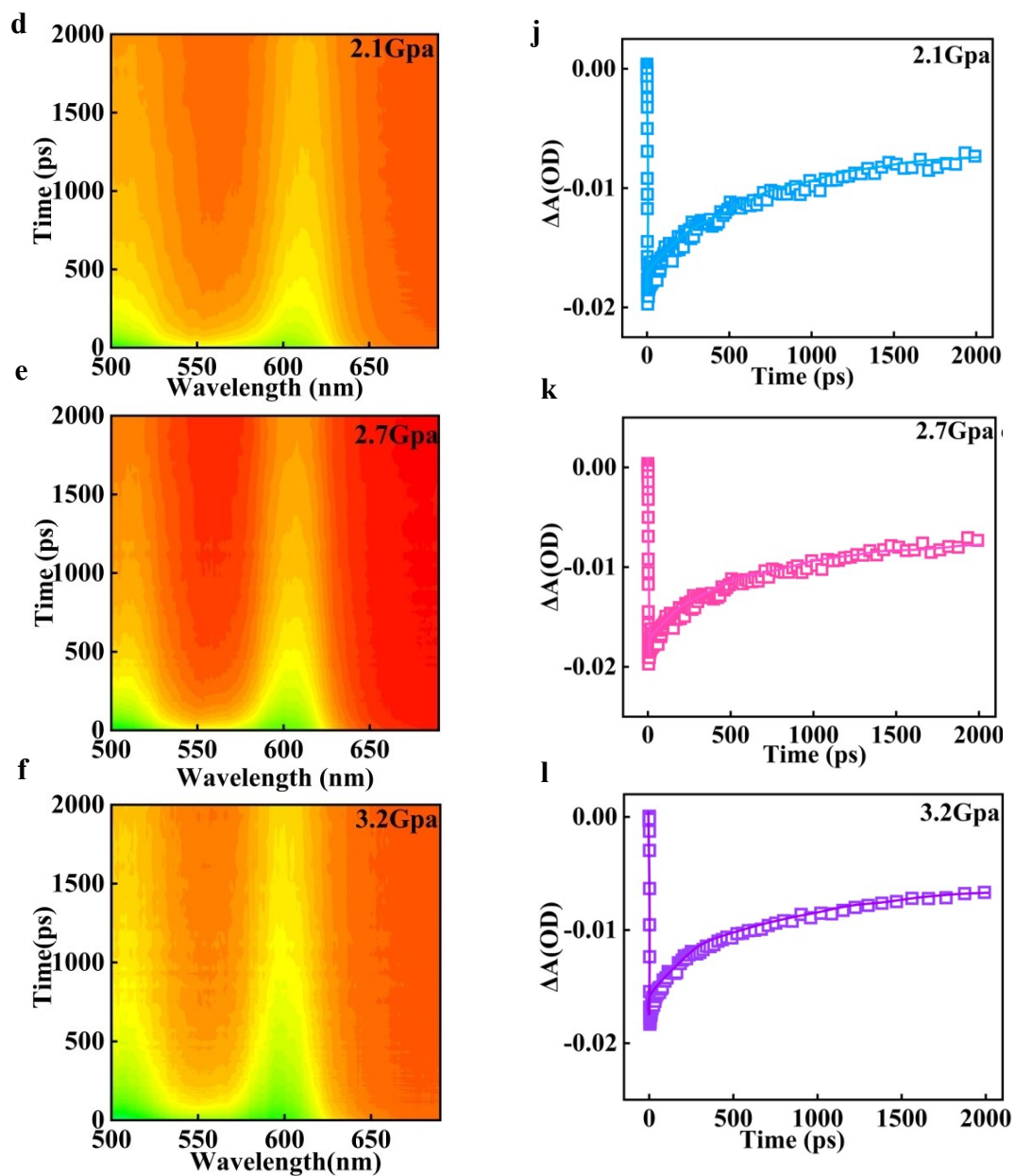
Fig. S3 (a-f) Transient absorption spectra of QD-Rh640 complexes in aqueous solution with pressure from 0.9 to 3.2 GPa. (g-l) Kinetics of Transient absorption spectraof QD-Rh640 complexes at corresponding pressures. The solid lines correspond to the fittings.

Table S2 Lifetimes of the QD-Rh640 complexes at different pressures. The carrier relaxation (τ_1), Fluorescence resonance energy transfer (τ_2) and Auger recombination (τ_3) lifetime constants were presented respectively.

Pressure (GPa)	τ_1(ps)	τ_2(ps)	τ_3(ps)
1atm	0.715±0.170		437.4±37.600
0.3	0.625±0.130	60.325±11.801	445.4±70.612
0.7	0.523±0.211	37.738±9.322	459.7±37.507
0.9	0.493±0.290	28.531±5.967	465.1±66.536
1.2	0.392±0.501	20.421±3.521	472.0±126.458
1.8	0.405±0.403	16.032±4.236	480.6±157.041
2.1	0.433±0.189	11.235±3.458	496.3±36.226
2.7	0.568±0.336	8.464±2.897	492.7±28.547
3.2	0.601±0.103	5.338±1.980	510.1±141.500
3.6	0.614±0.109	5.163±1.321	519.3±134.500

The probability of finding a QD with n (molar ratio of donor and acceptor) adsorbed acceptor, p, is given by equation 3, where λ is the mean number of acceptor adsorbed to the QDs.[4]
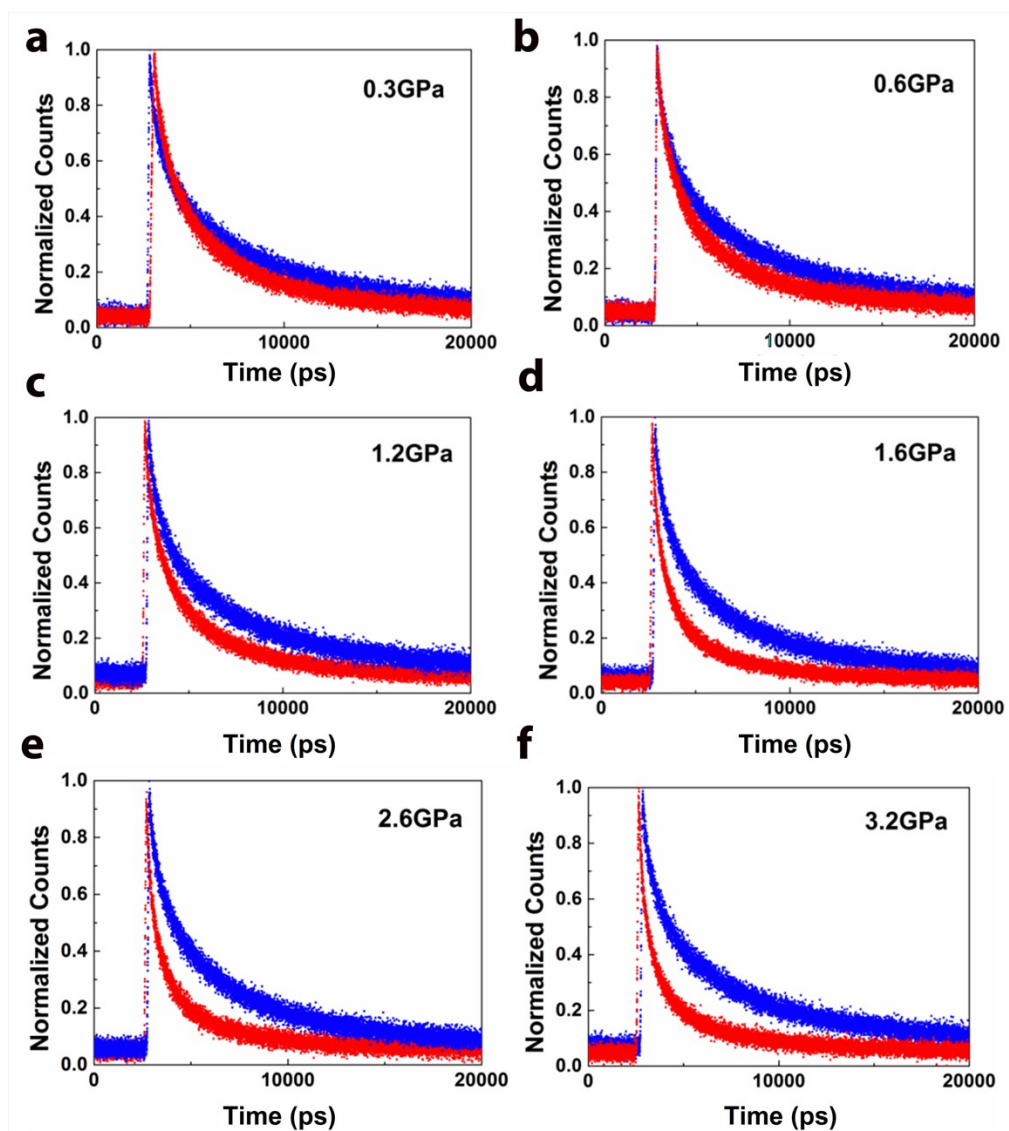
$$p(n, \lambda) = \frac{\lambda^n}{n!} e^{-\lambda}$$ (3)

We solve equation 1 for λ to yield equation 4.

$$\lambda = -\ln(B_v/B_0)$$ (4)

where B_v/B_0 is a ratio of the amplitude of the ground state bleach of the QD with added Rh640 dye (B_v) to that of the sample with no added Rh640 dye (B_0), for the complexes

under different pressure.

Fig. S4 Time resolved PL decay curves of QD alone and complexes in aqueous solution with pressure from 0.3 to 3.2 GPa. The blue lines represent the decay curve of QDs, and the red lines represent the decay curve of the complexes.

Table S3 Lifetimes of the QD and QD-Rh640 complexes at different pressures. The Auger recombination lifetime (τ_1), fluorescence lifetime of QD (τ_2) and fluorescence lifetime of Rh640 (τ_3) were presented respectively.

	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
0.3GPa QD	0.45±0.12	4.23±0.78	
0.3GPa Complexes	0.49±0.20	3.61±1.12	13.10±0.78
0.6GPa QD	0.46±0.14	3.83±0.42	
0.6GPa Complexes	0.41±0.18	3.15±1.20	12.73±1.79
1.2GPa QD	0.49±0.16	3.36±0.50	
1.2GPa Complexes	0.45±0.18	2.34±0.52	10.14±0.50
1.6GPa QD	0.50±0.10	3.03±0.59	
1.6GPa Complexes	0.48±0.11	1.54±0.42	9.23±2.92
2.6GPa QD	0.52±0.04	2.88±0.15	
2.6GPa Complexes	0.52±0.10	1.15±0.12	8.14±1.50
3.2GPa QD	0.55±0.09	2.73±0.72	
3.2GPa Complexes	0.53±0.12	0.81±0.58	7.80±0.97

TRPL measurements analysis: The addition of Rh640 reduces the fluorescence lifetime of QDs, and with the increase of pressure, the degree of reduction of the fluorescence lifetime increases (Fig. S4). Meanwhile, the degree of FRET-induced-reduced fluorescence lifetime of QDs gradually increase as increasing pressure (Table S3). These prove that FRET occurs and as the pressure increases, the efficiency of energy transfer increases.

References

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