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

Investigation on the photoinduced chemical reaction between p-benzoquinone and tryptophan in homogeneous solution

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1. The instrument structure of time-resolved electron paramagnetic resonance

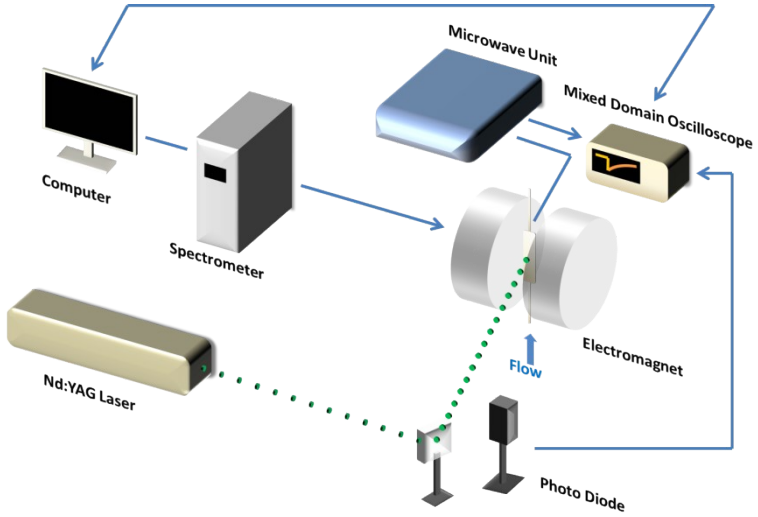

Figure S1. Composition of time-resolved electron paramagnetic resonance.

2. EPR spectral lines

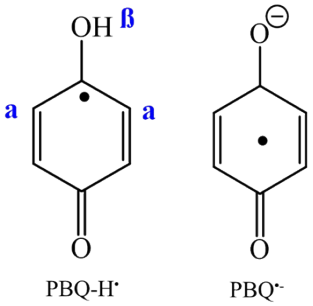

Figure S2. The structures of PBQ+H• and PBQ•-.

For 1,4-benzosemiquinone radical (PBQ+H•), only one unpaired electron and two groups equivalent nuclei ($I = \frac{1}{2}$). Under the strong external magnetic field, the contribution of nuclear Zeeman term may be ignored, the Hamiltonian of the first-order approximation is

$$\hat{H} = g\beta H\hat{S}_z + \hat{S}_z\left(a_\alpha \hat{I}_{1z} + a_\alpha \hat{I}_{2z} + a_\beta \hat{I}_z\right) \quad (1)$$

$$E = \left\langle M_S, M_{I1}^{(\alpha)}, M_{I2}^{(\alpha)}, M_I^{(\beta)} \middle| \hat{H} \middle| M_S, M_{I1}^{(\alpha)}, M_{I2}^{(\alpha)}, M_I^{(\beta)} \right\rangle = g\beta H M_S + M_S\left(a_\alpha M_{I1}^{(\alpha)} + a_\alpha M^{(}\right.$$
$$\equiv g\beta H M_S + M_S\left(a_\alpha M_\alpha + a_\beta M_\beta\right) \quad (2)$$

Where the M_α and M_β are: $M_\alpha = M_{I1}^{(\alpha)} + M_{I2}^{(\alpha)}, M_\beta = M_I^{(\beta)}$, and the selection rule is $\Delta M_S = 1,\ \Delta M_{I1}^{(\alpha)} = 0,\ \Delta M_{I2}^{(\alpha)} = 0,\ \Delta M_I^{(\beta)} = 0$. Add the microwave of υ, equation (2) can be expressed as:

$$h\nu = \Delta E = g\beta H + [a_\alpha\left(M_{I1}^{(\alpha)} + M_{I2}^{(\alpha)}\right) + a_\beta M_I^{(\beta)}] \quad (3)$$

make $\frac{h\nu}{g\beta} \equiv H_0$, $\frac{a_\alpha}{g\beta} \rightarrow a_\alpha^{'}$, $\frac{a_\beta}{g\beta} \rightarrow a_\beta^{'}$, equation (3) can be simplified to

$$H = H_0 - [a_\alpha^{'}\left(M_{I1}^{(\alpha)} + M_{I2}^{(\alpha)}\right) + a_\beta^{'} M_I^{(\beta)}] \quad (4)$$

Moreover, the $M_{I1}^{(\alpha)} + M_{I2}^{(\alpha)}$ can be taken as $1, 0, -1$, and $M_I^{(\beta)}$ is $\frac{1}{2}$ or $-\frac{1}{2}$, we can get 3×2 = 6 spectral lines. The $\left(M_{I1}^{(\alpha)} = +\frac{1}{2}, M_{I2}^{(\alpha)} = +\frac{1}{2}, M_I^{(\beta)} = +\frac{1}{2}\right)$ can be expressed as $(+,+,+)$, and the resonant magnetic field of these six spectral lines can be expressed as:

$H_1 = H_0 - a_\alpha^{'} - \frac{1}{2}a_\beta^{'}$: $(+,+,+)$

$H_2 = H_0 - a_\alpha^{'} + \frac{1}{2}a_\beta^{'}$: $(+,+,-)$

$H_3 = H_0 - \frac{1}{2}a_\beta^{'}$: $(+,-,+),(-,+,+)$

$H_4 = H_0 + \frac{1}{2}a_\beta^{'}$: $(+,-,-)(-,+,-)$

$H_5 = H_0 + a_\alpha^{'} - \frac{1}{2}a_\beta^{'}$: $(-,-,+)$

$H_6 = H_0 + a_\alpha^{'} + \frac{1}{2}a_\beta^{'}$: (−, −, −)

In summary, the intensity ratio of six spectral lines is 1: 1: 2: 2: 1: 1.

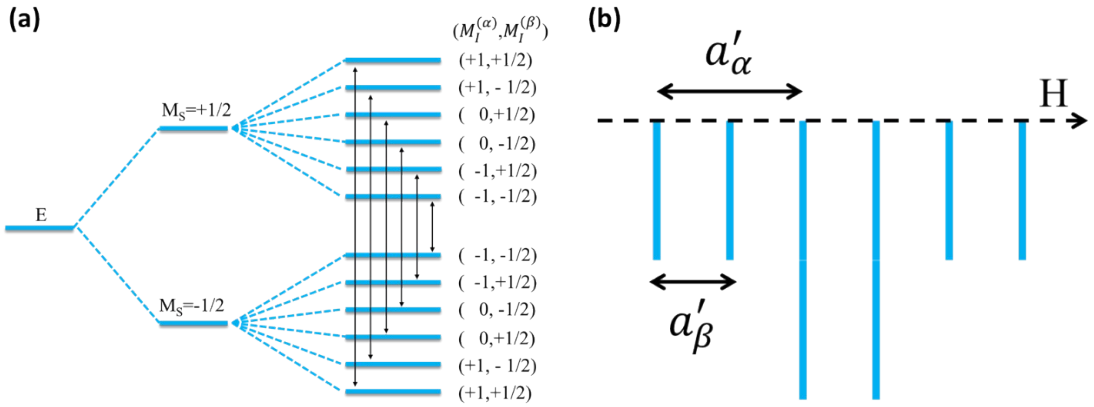

Figure S3. (a) Energy levels and allowable transitions of PBQ+H• in the fixed microwave frequency. (b) Stick spectrum of PBQ+H• in the fixed microwave frequency.

For PBQ•-, one unpaired electron and four equivalent nuclei ($I = \frac{1}{2}$):

$$\hat{H} = g\beta H\hat{S}_z + \hat{S}_z \sum_{i=1}^{4} a_i \hat{I}_{iz} \tag{5}$$

The eigenfunction is $|M_s, M_{I1}, M_{I2}, M_{I3}, M_{I4}\rangle$, that $M_s, M_{I1}, M_{I2}, M_{I3}, M_{I4}$ may be selected to $\pm\frac{1}{2}$. And the energy of PBQ•- is:

$$E(M_s, M_{I1}, M_{I2}, M_{I3}, M_{I4})$$

$$= \langle M_s, M_{I1}, M_{I2}, M_{I3}, M_{I4}|\hat{H}|M_s, M_{I1}, M_{I2}, M_{I3}, M_{I4}\rangle = g\beta H M_s + M_s\left(\sum_{i=1}^{4} a_i M_{Ii}\right) \tag{6}$$

Based on the conservation law of angular momentum, the selection rule is $\Delta M_S = 1,\ \Delta M_{Ii} = 0\ (i = 1,2,3,4)$. Thus:

$$\Delta E = g\beta H + \sum_{i=1}^{4} a_i M_{Ii} \tag{7}$$

According to the resonance condition under the microwave of υ: $h\nu = \Delta E$, the equation (7) can be expressed as:

$$h\nu = g\beta H + \sum_{i=1}^{4} a_i M_{Ii} \quad \text{or} \quad H = \frac{h\nu}{g\beta} - \sum_{i=1}^{4} \frac{a_i}{g\beta} M_{Ii} \tag{8}$$

make $\frac{h\nu}{g\beta} \equiv H_0$, $\frac{a_i}{g\beta} \rightarrow a_i^{'}$, equation (8) can be expressed as:

$$H = H_0 - \sum_{i=1}^{4} a_i^{'} M_{Ii} \tag{9}$$

The unpaired electron and four protons on the benzene unit are the equivalent coupling. Thus, $a_1^{'} = a_2^{'} = a_3^{'} = a_4^{'} = a$, and $H = H_0 - a\sum_{i=1}^{4} M_{Ii}$. So, $\sum_{i=1}^{4} M_{Ii}$ can be taken as 2, 1, 0, -1, -2, and the $\left(M_{I1} = +\frac{1}{2}, M_{I2} = +\frac{1}{2}, M_{I3} = +\frac{1}{2}, M_{I4} = +\frac{1}{2}\right)$ can be expressed as $(+,+,+,+)$, the resonant magnetic field of these five spectral lines can be expressed as:

$H_1 = H_0 - 2a$: $(+,+,+,+)$

$H_2 = H_0 - a$: $(-,+,+,+)(+,-,+,+)(+,+,-,+)(+,+,+,-)$

$H_3 = H_0$: $(-,-,+,+)(-,+,-,+)(-,+,+,-)(+,-,-,+)(+,-,+,-)(+,+,-,-)$

$H_4 = H_0 + a$: $(+,-,-,-)(-,+,-,-)(-,-,+,-)(-,-,-,+)$

$H_5 = H_0 + 2a$: $(-,-,-,-)$

In summary, the line distance between two adjacent spectral lines is a, and the intensity ratio is 1: 4: 6: 4: 1.

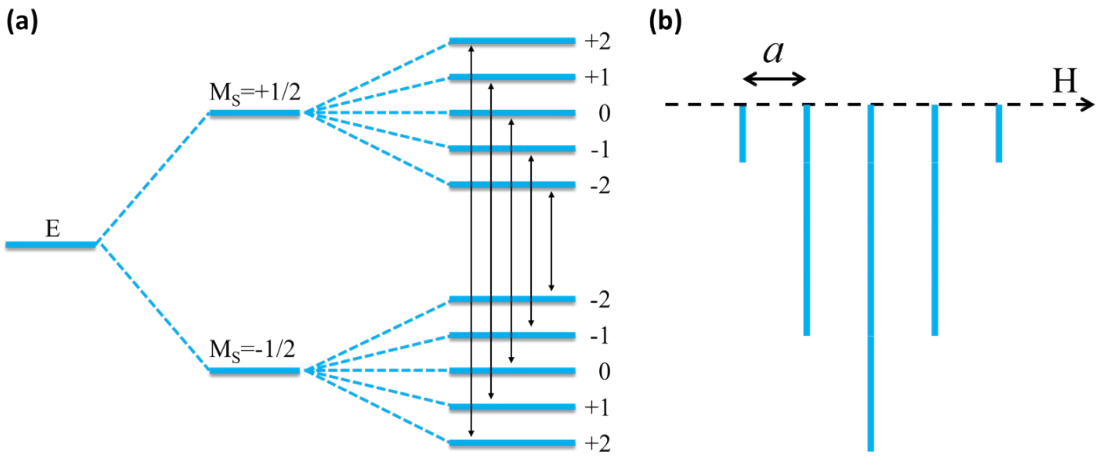

Figure S4. (a) Energy levels and allowable transitions of $PBQ^{\bullet-}$ in the fixed microwave frequency. (b) Stick spectrum of $PBQ^{\bullet-}$ in the fixed microwave frequency.

3. The theoretical calculation results.

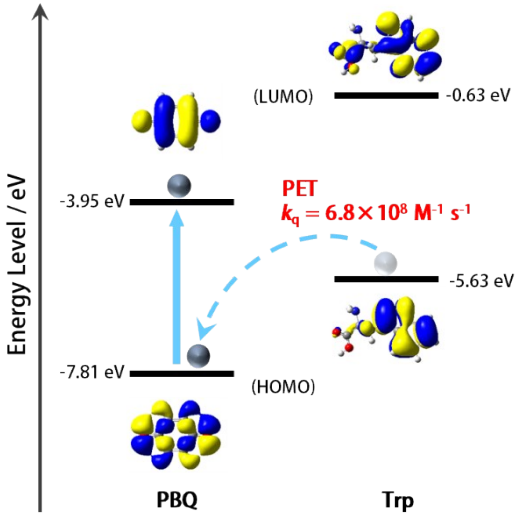

Figure S5. The PET from Trp to PBQ.

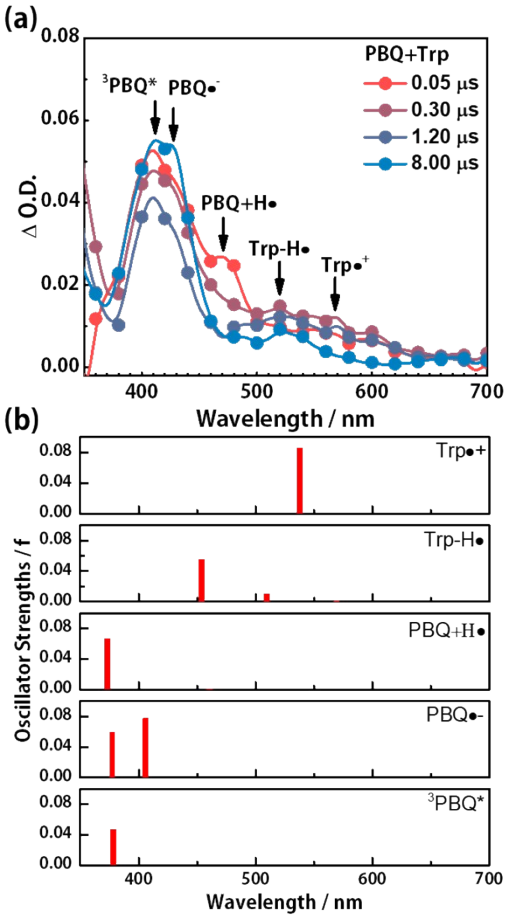

Figure S6. (a) Nansecond transient absorption spectra of PBQ and Trp in EG/H_2O solution. (b) The triplet-triplet transition absorption states ($T_1 \rightarrow T_n$) of ^{3}PBQ*, PBQ$^{\bullet-}$, PBQ+H$^\bullet$, Trp-H$^\bullet$ and Trp$^{\bullet+}$ by DFT and TDDFT calculations.

Table S1. Theoretical calculation results of triplet-triplet transition absorption states ($T_1 \rightarrow T_n$) .

Trp$^{\bullet+}$		Trp-H$^\bullet$		PBQ+H$^\bullet$		PBQ$^{\bullet-}$		^{3}PBQ*	
Energy / nm	f	Energy / nm	f	Energy / nm	f	Energy / nm	f	Energy / nm	f
1048.28	0.0003	893.91	0.0002	**460.52**	**0.0011**	**405.92**	**0.0774**	434.53	0.0001
989.96	0.0106	569.29	0.0009	373.23	0.0666	377.4	0.0594	**378.23**	**0.0467**
537.82	**0.0856**	**509.42**	**0.0103**	308.9	0.0587	285.98	0.0795	326.31	0.0227
420.21	0.0001	453.93	0.0548					318.19	0.0123
346.77	0.0002	328.08	0.0096						
336.57	0.0088	307.07	0.0352						
313.38	0.0747	□	□						

4. The bimolecular quenching rate constant

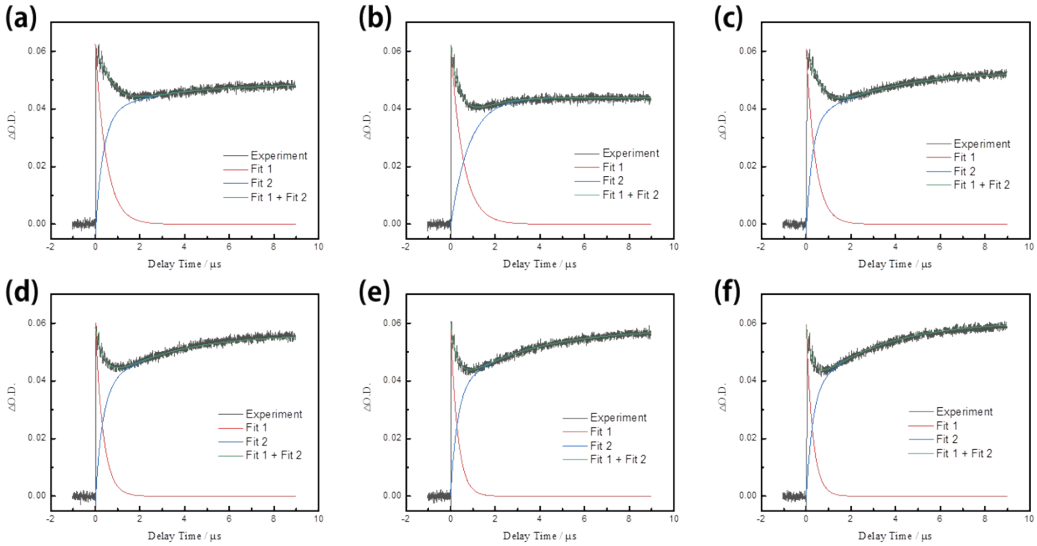

Figure S7. Decay kinetic curves of ^{3}PBQ* measured at 410 nm with different concentrations of Trp. (a) 0 mM, (b) 0.5 mM, (c) 1.0 mM, (d) 1.5 mM, (e) 2.0 mM, (f) 2.5 mM.

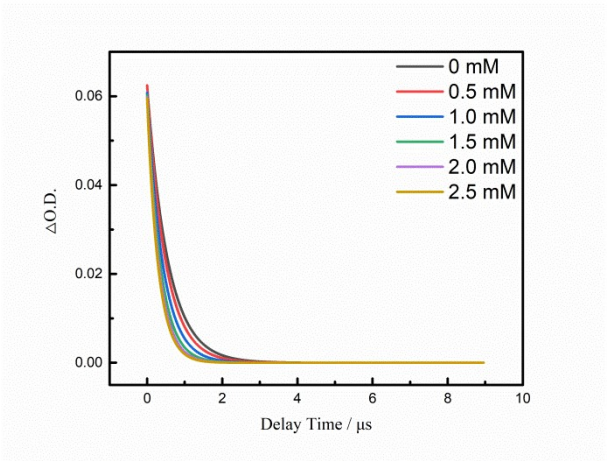

Figure S8. The decay kinetic curves of ^{3}PBQ* at 410 nm was obtained by global fitting.