



Study of one-step photosynthesis of Ag nanoparticles

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ABSTRACT

During photosynthesis of metal nanoparticles (NPs) in aromatic ketone systems, the aromatic ketone triplets are explored as hydrogen atom/electron abstractors which yield highly reactive radicals. However, their electron donation ability is sparsely recognized. Here we report the investigations of benzophenone (BP)-initiated one-step photosynthesis of Ag NPs in H donor free system using spectroscopic and theoretical methods. Experimentally, the direct observations of BP cation radical ($\text{BP}^{+\cdot}$) and Ag NPs *via* transit and steady-state absorption spectroscopy demonstrate the electron donation ability of BP triplets which directly reduce Ag^+ to Ag^0 . In the following reactions, both theoretical calculation and experimental results reveal that the generated $\text{BP}^{+\cdot}$ recovers itself to BP by grabbing an electron from NO_3^- and the generated nitrate radicals (NO_3^\cdot) then decay to nitrogen oxides. Notably, BP plays a role as photocatalyst in our system. This study details the mechanism of one-step photosynthesis of Ag NPs which provides a new insight of aromatic ketones in photochemistry and may offer a facile approach to photosynthesis of metal NPs.

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1. Introduction

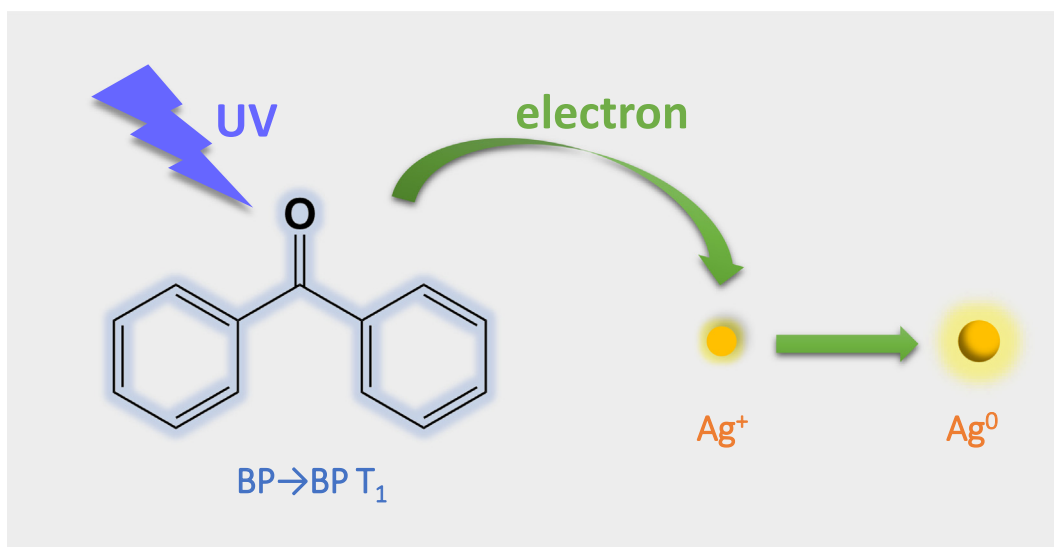
Noble metal NPs is in great demand [1,2] because of their excellent properties and wide use in energy production [3–5], biological molecules detection [6–8] and medical treatment [9–11]. Due to surface plasma resonance effect, spectroscopic method has been used to detect noble metal NPs by measuring surface plasmon band (SPB) absorbance. As a popular class of photosensitizer for metal NPs photosynthesis, aromatic ketones have attracted extensive attention for strong absorption in ultraviolet [12–17] and high efficiency of intersystem crossing (ISC) [18–20]. Moreover, the characteristic of efficient photon-induced electron transfer (ET) [21–24] makes aromatic ketones a preferred photoinitiator in photochemistry field. From previous studies, with the presence of hydrogen atom/electron donors (eg: ethanol, trimethylamine, polyvinyl pyrrolidone, etc), aromatic ketone triplets exhibit strong hydrogen atom/electron abstraction ability [1–3,25–29]. The generated highly reactive radicals after hydrogen atom/electron transfer are favorable specials in photosynthesis of metal NPs. To explore and improve radical's performance and generation quantum yield, most works focused on their electron/hydrogen atom abstraction property. As a result, electron donating ability of aromatic ketone triplets is barely recognized and reported.

Benzophenone (BP) which is the typical and peculiar aromatic ketone photosensitizer, has simple structure and extraordinary high efficiency of ISC ($\Phi_{\text{ISC}} \sim 1$) [18]. This character makes BP especially suited for triplet state study using ultrafast transient absorption (TA) spectroscopy. In 2005, Farid and co-workers described BP triplets as electron donor in study of chain-amplified photoreactions and assigned TA peak at 390 nm to $\text{BP}^{+\cdot}$ for the first time. [30] Later in 2013, Scaiano's group reported the potential role of BP triplets as reducer in the system containing H_2O . [31] This makes electron donation property of BP triplets in H donor-free systems for metal NPs synthesis remains unclear.

In this work, combining experimental and theoretical methods, we systematically studied the mechanism of BP-initiated one-step photosynthesis of Ag NPs in simple system of BP with AgNO_3 (Scheme 1). AgNO_3 was chosen for its suitable reduction potential which is $E_{\text{Ag}^+} = 0.799 \text{ V}$ at 20°C . [32] To eliminate possible effect of H_2O as an H donor, all samples are prepared in super-dry acetonitrile (ACN). After excitation (@355 nm), BP goes through highly efficient ISC process and yields BP triplet ($\text{BP } T_1$). Electron donating process of BP T_1 was quantified using nanosecond TA spectroscopy in which the formation and decay processes of $\text{BP}^{+\cdot}$ were directly detected. Silver NPs formation was explored *via* UV–Vis absorbance spectra. In the following reactions, time-dependent density functional theory (TDDFT) and density functional theory (DFT) calculations were conducted to study $\text{BP}^{+\cdot}$ decay process after electron donating of BP triplets. Moreover, to figure out all radical decay pathways, high performance liquid chromatography (HPLC) and chemisorption analysis experiments were also performed to verify the final products in both liquid and gas phases.

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Scheme 1. Benzophenone structure and Ag NPs photosynthesis processes in BP-AgNO₃ system.

2. Experimental Section

2.1. Chemicals

Benzophenone (BP, 99%, Alfa Aesar); Silver Nitrate (AgNO₃, 98%, Kermel); Acetonitrile (ACN, 99.9%, super-dry, water < 30 ppm, J&K). All chemicals are used without further purification.

2.2. Experimental Setup

UV–Vis absorbance spectra of Ag NPs SPB were measured using PerkinElmer Lambda 35 UV–Vis spectrometer. The ultrafast nanosecond TA spectra and kinetics measurements were performed by time-resolved laser flash photolysis system. HPLC was measured using Agilent 1290 Infinity LC (6540 QTOF). The chemisorption analysis experiments were carried out by AutoChem 2910.

3. Theoretical Methods

TDDFT and DFT methods were used by Gaussian 09 programs [33] for simulations of BP T₁-Ag⁺ complex and BP⁺⁺-NO₃⁻ complex, respectively. Functional used is B3LYP. For basis set, 6-311++G(d,p) was chosen for C/H/O/N and LANL2DZ was used for Ag⁺ because it is proper basis set for an ionic compound. Solution effect has also been considered by which CPCM model was used for solvent correction of acetonitrile.

4. Results and Discussion

4.1. UV–Vis Absorbance Spectra of Ag NPs SPB

To validate the photosynthesis of Ag NPs in the system of BP and AgNO₃ in super-dry ACN, UV–Vis absorbance spectra of Ag NPs SPB was measured. SPB position of Ag NPs with the diameter range of 10–100 nm is at 400–420 nm [34–37]. As shown in Fig. 1(a), after excitation (@355 nm), a broad peak shows up from 400 nm to 700 nm and the strongest Ag NPs SPB absorbance peak arises at 422 nm. The Ag NPs SPB absorbance grows with the increase of laser irradiation time from 0 to 40 min, this indicates continuous generation of Ag NPs. The TEM image of Ag NPs can be found in Fig. S1. For a quantitative view, the absolute integrated area of absorbance from 400 nm to 450 nm at different irradiation time in Fig. 1(a) was calculated and shown in Fig. 1(b). We

notice that although the formation of Ag NPs increases with illumination time, the generation rate decreases. This is likely due to blocking of excitation photon by silver ‘mirror’: after long-time irradiation, considerable amount of Ag NPs has attached to the internal surface of cuvette which reduce excitation power (see S12). Furthermore, to eliminate effect of ACN on Ag NPs synthesis, reference experiments of pure AgNO₃ in super-dry ACN were carried out and result is shown in Fig. S3. It demonstrates that Ag NPs would not be produced under 355 nm irradiation without BP. Herein, BP plays the key role in photosynthesis of Ag NPs and BP T₁ tends to be the electron donor.

4.2. Observation of BP⁺⁺ via TA Spectroscopy

Experimentally, when considering BP T₁ as the electron donor for Ag NPs synthesis, BP⁺⁺ should be detected. Based on previous paper, the TA characteristic peak of BP⁺⁺ located at ~390 nm.³⁰ Here we conduct nanosecond TA measurement. As shown in Fig. 1(c), a strong absorption peak at 380 nm is detected and we would assign it to BP⁺⁺ since no species in system has absorption at this wavelength. It shows that BP⁺⁺ was formed rapidly in the first 0.124 μs which indicates the ultrafast electron transfer from BP T₁ to Ag⁺. Then the signal of BP⁺⁺ decays to zero within 5 μs. To study its dynamic characteristic, kinetics of BP⁺⁺ at 380 nm was shown and fitted by mono-exponential function. As shown in Fig. 1(d), the obtained lifetime of BP⁺⁺ is 2.166 ± 0.102 μs with the adjusted R² = 0.82. The direct observation of BP⁺⁺ via TA spectra verifies the electron donating ability of BP T₁ in H donor-free system.

4.3. Theoretical Simulation of BP T₁-Ag⁺ Interaction

To better understand the pathway of electron transfer from BP T₁ to Ag⁺, TDDFT calculation of total energy scan was conducted. As shown in Fig. 2, when the distance between Ag⁺ and O (BP T₁) is larger than 3.00 Å, reaction would not take place. When they get closer, total energy begins to increase. To accomplish ET, an energy barrier of 9.13 kcal/mol has to be overcome at distance of 2.45 Å. At room temperature, reaction which has energy barrier lower than 21 kcal/mol is considered as a spontaneous reaction.² Therefore, it is reasonable that BP T₁ reduces Ag⁺ with the 9.13 kcal/mol energy barrier. Moreover, a total energy loss of 5.81 kcal/mol after ET can facilitate this process by which BP⁺⁺-Ag⁰ complex turns into a relatively stable state. This result supports the observation of electron donation from BP T₁ to Ag⁺.

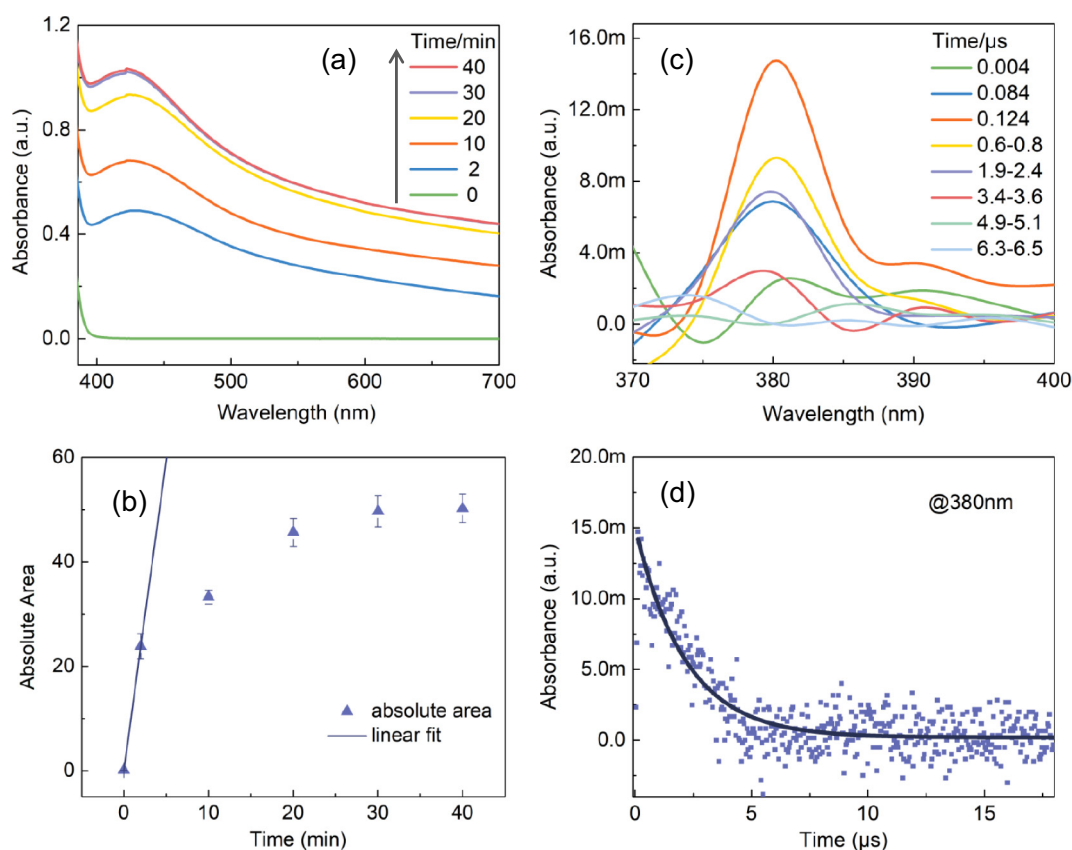


Fig. 1. (a) UV–Vis absorbance spectra of Ag NPs surface plasmon band (SPB) for sample of BP and AgNO₃ under excitation for different irradiation time (0–40 min); (b) Integrated absolute area of Ag NPs absorbance from 400 to 450 nm in (a) as function of irradiation time, triangles are the data points and solid line is the linear fit of first 2 points at irradiation time of 0 and 5 min, respectively; (c) Nanosecond TA spectra from 0.004 μs to 6.5 μs under excitation; (d) Kinetic curve of BP^{•+} at 380 nm, blue dots are raw data and red line is its mono-exponential fit. Note: for all measurements, samples are prepared as BP (50 mM) and AgNO₃ (50 mM) in super-dry ACN; excitation wavelength is at 355 nm and set as 25 mJ/pulse.

4.4. Mechanism of Radical Decay

To reveal the mechanism of BP^{•+} decay after ET process, HPLC and chemisorption analysis experiments were carried out to exam the components in both liquid phase and gas phases, respectively. HPLC

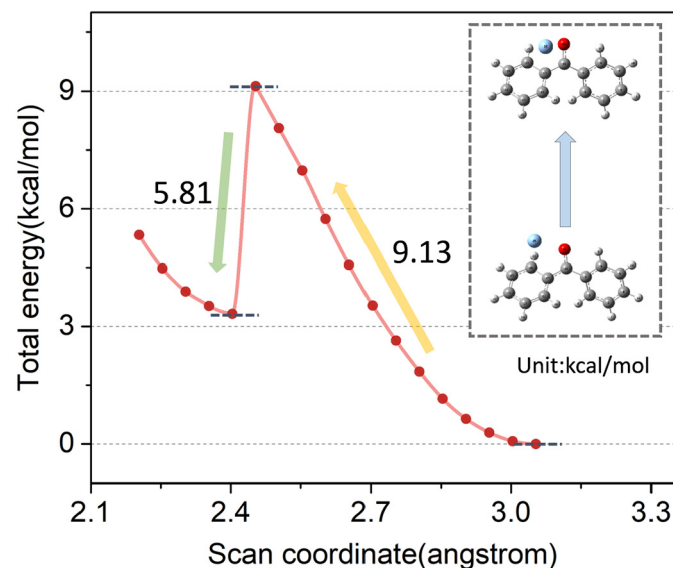


Fig. 2. Total energy scan of BP T₁ and Ag⁺ in ACN. Inset: configurations of BP T₁ and Ag⁺ before and after electron transfer process.

measurements of solution samples before and after laser irradiation under 355 nm are shown in Fig. 3(a). Without excitation, HPLC result shows two peaks arising at 10.377 min and 13.457 min (upper graph in Fig. 3(a)) and they can be ascribed to AgNO₃ and BP, respectively [1]. After 40 min irradiation, as shown in lower graph in Fig. 3(a), HPLC shows the same peaks at 10.385 min (AgNO₃) and 13.472 min (BP). This suggests that BP^{•+} does not decay by dissociating or dimerizing. As a result, the only decay pathway for BP^{•+} is to recover itself to BP by obtaining an electron from other component in solution.

Herein, we propose that BP^{•+} decays by electron abstraction from NO₃[−], after which BP and NO₃ radical are produced, then the unstable NO₃ radical decays to nitrogen oxides. To prove this proposal, chemisorption experiment was carried out to verify the nitrogen oxides products in gas phase. Given that trace nitrogen oxides may exist in purge gas (nitrogen) used during sample preparation, upper gas in both cuvettes with and without irradiation are tested and compared. As shown in Fig. 3(b), for sample without irradiation, it shows trace NO and no N₂O/NO₂ in purge gas. However, after irradiation for 40 min, abundant NO and N₂O are produced. For quantitative comparison, integrations of all peaks are listed in Table S1 and it indicates that NO is the primary product. Here the generation of nitrogen oxides proves that NO₃[−] is decomposed in the presence of BP^{•+} which supports the proposal. More information of chemisorption experiment is shown in supporting information (SI4).

4.5. Theoretical Simulation of BP^{•+}–NO₃[−] Interaction

To further study the interaction between BP^{•+} and NO₃[−], we conducted DFT calculation and compared the energy of BP^{•+}–NO₃[−]

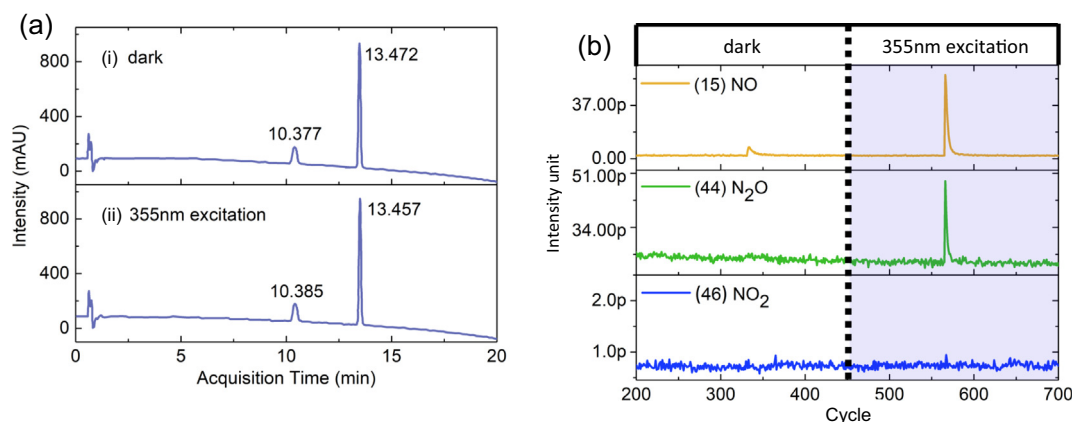


Fig. 3. (a) HPLC of samples solution (BP, 50 mM; AgNO₃, 50 mM, in super-dry ACN) (i) before and (ii) after laser irradiation; (b) Chemisorption analysis of nitrogen oxides before (200–400 cycles) and after (450–700 cycles) excitation. Laser excitation wavelength is 355 nm with the power of 25 mJ/pulse and irradiation time is set as 40 min for both experiments.

complex before and after electron transfer from NO₃[−] to BP⁺⁺. As shown in Fig. 4(a), after optimizing BP⁺⁺–NO₃[−] complex at the relatively long distance of 4.00 Å (between O atoms from BP⁺⁺ and NO₃[−]), a more stable configuration of BP–NO₃ complex (D = 3.62 Å) was obtained with an energy loss of 11.133 kcal/mol. This result indicates that ET process from NO₃[−] to BP⁺⁺ is theoretically feasible. Based on that, we scan the total energy of BP⁺⁺–NO₃[−] complex along reaction pathway. As shown in Fig. 4(b), with approaching of BP⁺⁺ to NO₃[−], there is a 15.22 kcal/mol potential barrier for electron transfer from NO₃[−] to BP⁺⁺. It is lower than 21 kcal/mol, this enables BP⁺⁺ decay pathway as a favorable reaction at room temperature. Herein, theoretical calculation further confirms the mechanism of BP⁺⁺ decay in Scheme 2 (step 2).

5. Conclusions

In this work, we investigate the mechanism of BP-initiated one-step photosynthesis of Ag NPs in H donor free system. The

experimental detection of Ag NPs via UV–Vis absorbance spectra and BP⁺⁺ via ultrafast TA spectra proves that Ag NPs can be produced by directly ET from BP T₁ to Ag⁺ under UV excitation. This result is also supported by TDDFT calculation. In the following reactions, by theoretical calculations, HPLC and chemisorption experiments, we reveal the free radicals decay pathways which are summarized in Scheme 2 (Step 2&3): BP⁺⁺ decays to BP by grabbing an electron from NO₃[−] in solution and the generated NO₃ decays to nitrogen oxides such as N₂O, NO. This study clarifies the whole reaction processes in one-step photosynthesis of Ag NPs and provides new understanding of BP triplets as electron donor in H donor free system. Moreover, it may offer a new approach for efficient and green photosynthesis of metallic NPs in simple systems.

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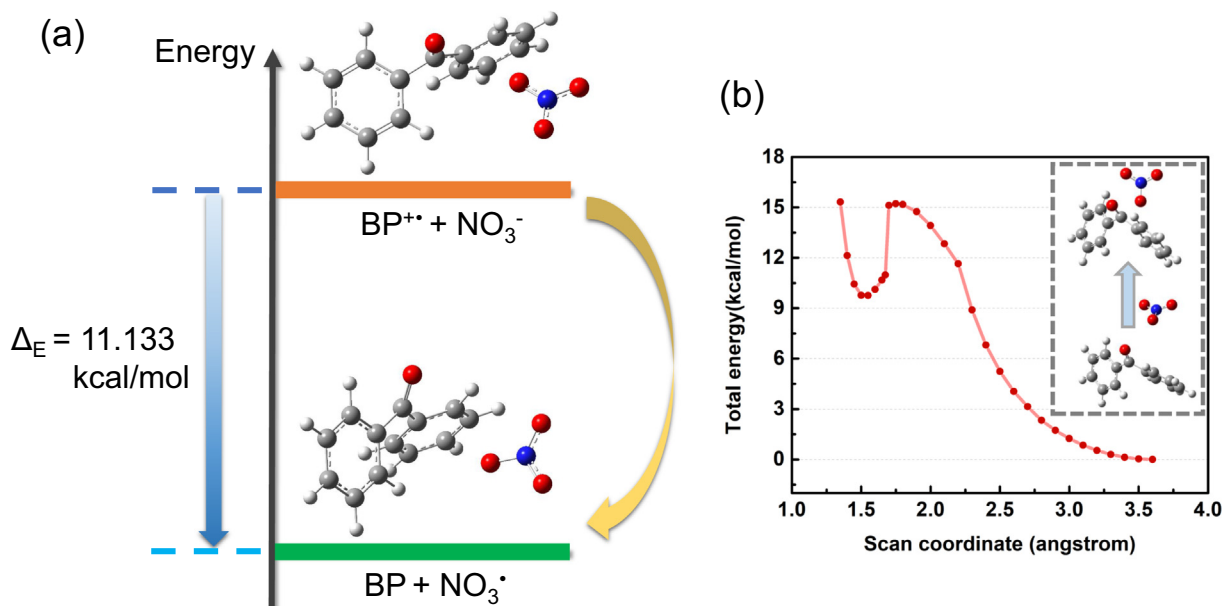
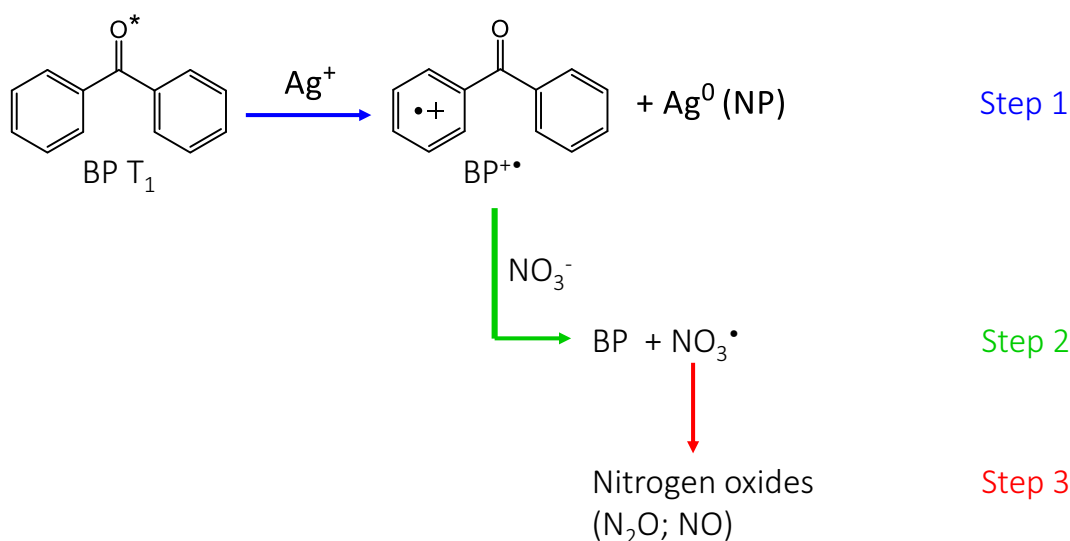


Fig. 4. (a) Energy calculation and optimized configurations of BP⁺⁺–NO₃[−] complex before and after electron transfer reaction. (b) Total energy scan of BP⁺⁺–NO₃[−] reaction pathway, inset is the configurations before and after electron transfer. Scan coordinate is the distance between O atom (BP⁺⁺) and O atom (NO₃[−]).



Scheme 2. Description of Ag NPs photosynthesis and radicals decay processes in H donor free system after 355 nm excitation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.saa.2018.05.089>.

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