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ARTICLE

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Nitric oxide (NO) is a signaling molecule that has a variety of functions in the human body, but is difficult to apply in biological experiments or for therapeutic purposes because of its high reactivity and instability in the biological milieu. Consequently, photocontrollable NO releasers, which enable spatiotemporal control of NO release, have an important role to play in elucidating the functions of NO. Our group has developed visible-light-controllable NO-releasing molecules that contain a fluorescent dye structure as a light-harvesting antenna moiety and an *N*-nitrosoaminophenol structure as an NO-releasing moiety. Here, we aimed to construct an NO-generating system employing intermolecular photoredox reaction between the two separate components, since this would simplify chemical synthesis and make it easier to examine various dyes as antennae. For this purpose, we constructed polymer nanoparticles doped with both an *N*-methyl-*N*-nitroso-4-aminophenol (NAP, **1**) and an Ir(III) antenna complex (**2**, **3** or **4**) in order to dissolve in aqueous solution without co-solvent. These polymer nanoparticles released NO upon photoirradiation in vitro in the purple (400–430 nm) or blue (400–460 nm) wavelength region to activate the doped Ir(III) complex.

Introduction

Nitric oxide (NO) is a reactive, gaseous transmitter that has various biological activities[1], including roles in endothelial vasodilation[2], neuronal transmission[3], and immune response[4], though the mechanisms involved have not yet been fully identified. To aid research, various NO-releasing reagents have been developed as chemical tools for biological experiments. Photocontrollable NO releasers are particularly useful, because they enable spatiotemporally well-controlled NO release. Most conventional photocontrollable NO releasers release NO in response to ultraviolet (UV) light[5–8], but the low tissue penetration and potent cytotoxicity of UV are problematic. More recently, NO-releasing compounds that can be controlled by visible or near-infrared (NIR) light have also been developed[9–12]. For example, our group has developed visible-light-controllable NO releasers based on *N*-nitrosoaminophenol structure. These compounds, represented by NOBL-1[13] and NORD-1[14] (Scheme 1a), are composed of a fluorescent dye structure as an antenna moiety and an *N*-nitrosoaminophenol structure as an NO-releasing moiety. The photocontrollable NO release is based on intramolecular photoinduced electron transfer (PeT)[15], also known as photoredox reaction (Scheme 1b). Building on our earlier work, we hypothesized if the antenna moiety and NO-releasing moiety were separately doped in nanoparticles, photocontrollable NO release might occur via an intermolecular PeT process within the limited area of each nanoparticle. Recently, Hu *et al.* reported a red-light-controllable NO releaser based on triplet-triplet energy transfer (TTET) in micelles composed of polymers conjugated with an *N*-nitrosoamine-substituted coumarin dye structure and a Pd(II) porphyrin structure[16]. This can be controlled by NIR light, probably via photoredox reaction process, but preparation requires many steps, including the synthesis of polymers bearing both photoredox catalyst and *N*-nitrosoamine moieties. Instead, we focused on polymer dots (P-dots), which are nanoparticles dispersible in an aqueous solution, as a carrier of the PeT components[17]. P-dots can be prepared from commercially available organic polymers and doped with organic molecules or metal complexes by simple mixing, and we considered this would both simplify chemical synthesis and make it easier to examine various dyes as antennae. Here we prepared P-dots containing *N*-methyl-*N*-nitrosoaminophenol (NAP, **1**)[18] as the NO-releasing moiety, and various Ir complexes

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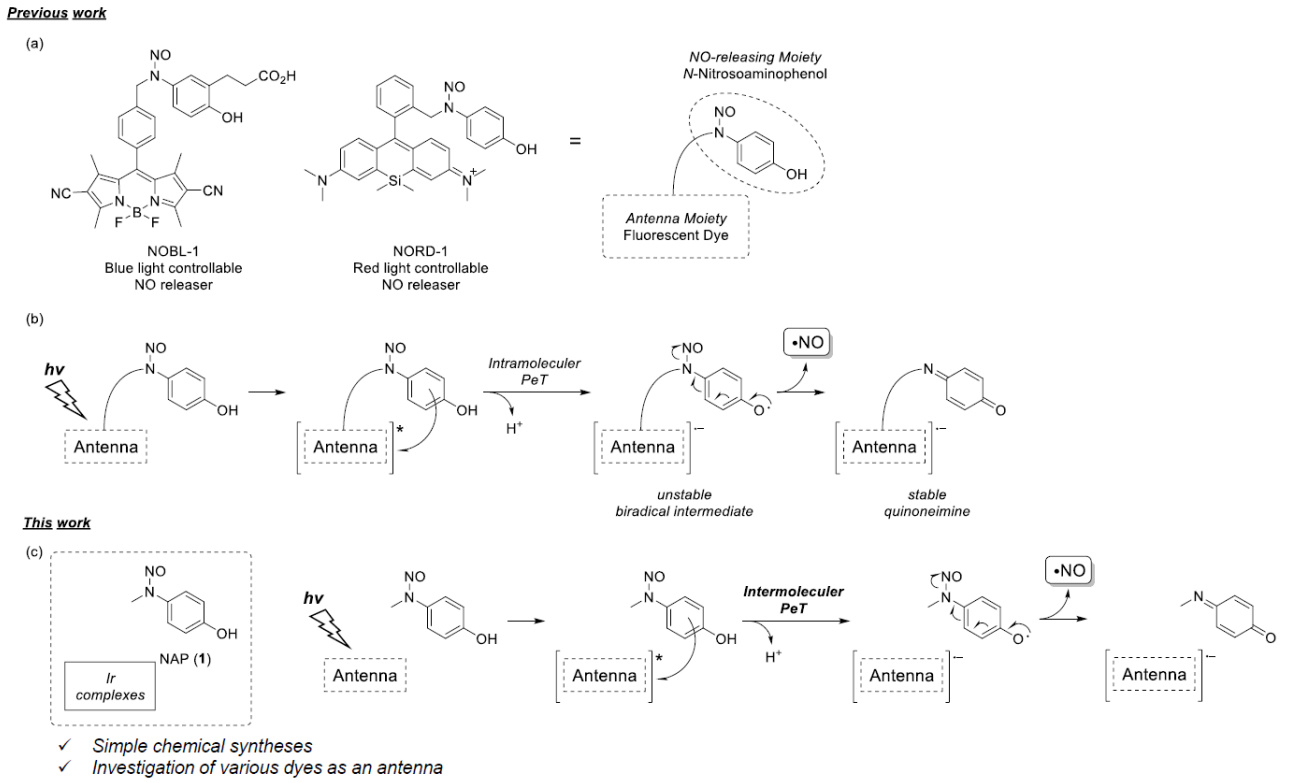


Scheme 1. (a) The structures of NOBL-1 and NORD-1, previously developed intramolecular-PeT-type NO releasers. (b) A plausible mechanism of photoinduced NO release from NOBL-1 or NORD-1. (c) The concept of this work and the hypothetical mechanism of photoinduced NO release driven by intermolecular PeT.

as the antenna moiety (Scheme 1c), and compared their photoinduced NO-releasing abilities by means of NO fluorescence probe and electron spin resonance measurements.

Experimental Methods

General Methods.

Ultraviolet-visible-light absorption spectra were recorded on an Agilent 8453 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5300PC spectrophotometer. Irradiation was conducted with a xenon lamp (MAX-302 or MAX-303, Asahi Spectra) equipped with an indicated band pass filter or an LED light source (CL-1501, Asahi Spectra) equipped with an indicated LED head. Dynamic light scattering measurements were performed using an FDLS-3000 system (Photal Co. Ltd.) equipped with a solid laser (100 mW, wavelength: 532 nm). All other reagents and solvents were purchased from Sigma-Aldrich, Polymer Source Inc., Tokyo Chemical Industry, FUJIFILM Wako Pure Chemical Corp., Nacalai Tesque, Kanto Chemical, Kishida Chemical, Junsei Chemical, or Dojindo and used without further purification. Flash column chromatography was performed using silica gel 60 (particle size 0.032–0.075 mm) supplied by Taiko Shoji. MPLC purification was performed using YFLC-Wprep2XY-S (Yamazen).

Measurements of Absorption and Fluorescence Spectra of 2–4.

Absorption spectra of solutions of **2**–**4** in THF were recorded. **2**: $Ir(dfppy)_2(B(pz)_4)PF_6$[19], **3**: $Ir(ppy)_2(pybi)PF_6$[20], **4**: $Ir(fpiq)_2(pybi)PF_6$.

Characterization of 2

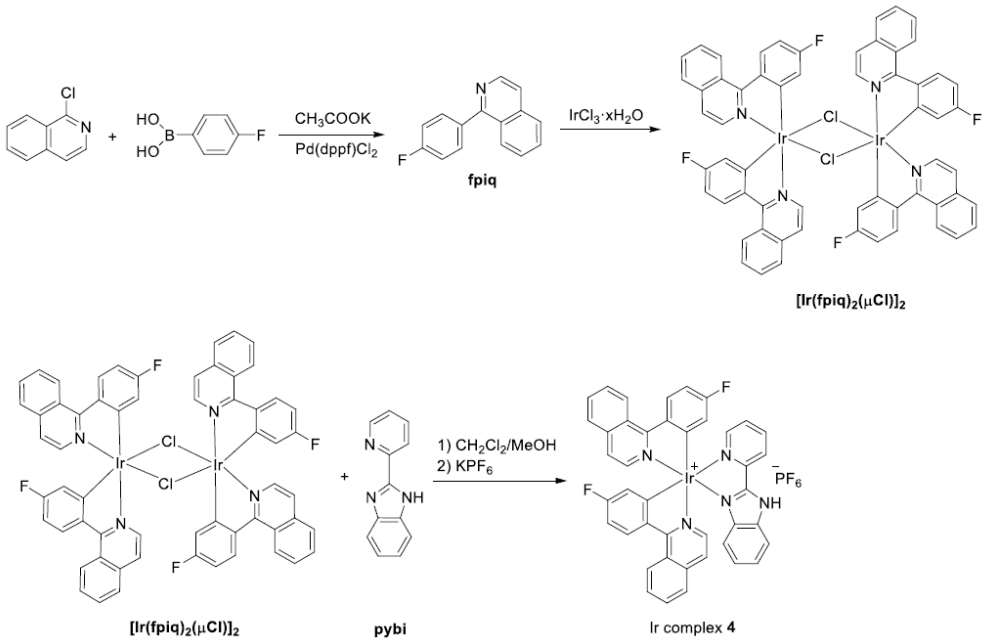
^{1}H NMR ($CDCl_3$, 400 MHz, δ; ppm) 8.17 (2H, d, *J* = 8.4 Hz), 7.71 (2H, d, *J* = 1.6 Hz), 7.62 (2H, td, *J* = 8.4 Hz, 1.6 Hz), 7.27 (2H, d, *J* = 0.8 Hz), 7.15 (2H, d, *J* = 2.4 Hz), 6.93 (2H, d, *J* = 1.2 Hz), 6.77–6.73 (2H, m), 6.50–6.43 (2H, m), 6.24 (2H, t, *J* = 2.0 Hz), 6.19 (2H, d, *J* = 2.4 Hz), 6.03 (2H, t, *J* = 2.0 Hz), 5.57 (2H, dd, *J* = 2.4 Hz, 8.8Hz) (Chart S1).

Characterization of 3

^{1}H NMR ($CDCl_3$, 400 MHz, δ; ppm) 8.83 (1H, d, *J* = 7.6 Hz), 8.09 (1H, t, *J* = 7.6 Hz), 7.91–7.80 (4H, m), 7.65–7.75 (6H, m), 7.49 (1H, d, *J* = 5.2 Hz), 7.38 (1H, t, *J* = 6.4Hz), 7.31 (1H, t, *J* = 7.6 Hz), 7.11–7.03 (2H, m), 7.00–6.92 (5H, m), 6.43 (1H, d, *J* = 7.6 Hz), 6.37 (1H, d, *J* = 7.2 Hz), 6.22 (1H, d, *J* = 8.0 Hz) (Chart S2).

Synthesis of 4 (Scheme 2)

Preparation of 1-(4-fluorophenyl)isoquinoline (fpiq)[21]**.** A Suzuki coupling reaction was employed. Typically, 1.1 g of 1-chloroisoquinoline (6.7 mmol), 1.0 g of 4-fluorophenylboronic acid (7.3 mmol), 34 mg of $Pd(dppf)Cl_2$ (catalyst) and 1.3 g of potassium acetate (base) were mixed in 30 mL of 1,4-dioxane (solvent). The



Scheme 2. Synthesis of Ir complex **4**.

reaction mixture was refluxed at 150 °C overnight under an argon atmosphere. After the reaction, the mixture was separated by using water/CH_2Cl_2. The organic phase was washed with saturated NaCl aqueous solution and DI water, dried over anhydrous Na_2SO_4 and evaporated under vacuum. Finally, the crude product was purified by silica column chromatography (hexane/ethyl acetate = 4/1).

Preparation of $[Ir(fpiq)_2(\mu Cl)]_2$[21]. 1-(4-Fluorophenyl)isoquinoline (fpiq) (2.6 mmol, 0.58 g) and $IrCl_3 \cdot xH_2O$ (0.25 g, 0.85 mmol) were dissolved in a mixture of water (5 mL) and 2-ethoxyethanol (15 mL). The reactants were refluxed at 120 °C under an argon atmosphere overnight. After the reaction, the mixture was cooled to room temperature. The red precipitate was collected, washed with water and diethyl ether, and used for the next step.

Preparation of 4. Typically, $[Ir(fpiq)_2(\mu Cl)]_2$ (0.20 mmol, 0.28 g) and ligand 2-(2-pyridyl)benzimidazole (pybi) (0.50 mmol, 0.10 g) were dissolved in 20 mL CH_2Cl_2/MeOH (1/1) and the solution was refluxed at 50 °C for 20 h. After cooling to room temperature, it was evaporated under vacuum. The residue was re-suspended in 2 mL of MeOH and dropped into 15 mL of KPF_6 aqueous solution (1.0 g, 5.4 mmol). The mixture was stirred for 10 min at room temperature, then the product was extracted with CH_2Cl_2. The organic solution was washed with saturated NaCl solution and DI water twice, dried over anhydrous Na_2SO_4 and evaporated under vacuum. Purification by silica column chromatography gave an orange solid (65%, 3 steps): ^{1}H NMR ($CDCl_3$, 500 MHz, δ; ppm) 8.90–8.84 (3H, m), 8.34–8.30 (2H, m), 7.96 (1H, dd, *J* = 7.6 Hz, 7.6 Hz), 7.87–7.69 (9H, m), 7.57 (1H, d, *J* = 6.6 Hz), 7.37 (1H, d, *J* = 6.4 Hz), 7.24–7.17 (3H, m), 6.94–6.82 (3H, m) 6.10 (1H, dd, *J* = 2.7 Hz, 9.3 Hz), 6.06–6.03 (2H, m) (Chart S3); ^{13}C NMR ($CDCl_3$, 125 MHz, δ; ppm) 168.10, 167.93, 164.75, 164.12, 162.71, 162.08, 149.79, 142.30, 142.26, 142.25, 141.26, 140.22, 138.96, 136.99, 136.74, 132.29, 132.21, 131.91, 131.83, 131.55, 131.45, 128.61, 128.57, 127.62, 127.40, 126.61, 126.46, 125.99, 125.96, 123.37, 121.56, 121.20, 119.08, 118.94, 118.60, 118.46, 116.84, 116.07, 109.24, 109.11, 109.06, 108.93 (Chart S4); HRMS (ESI-pos) calcd: 832.18637; found 832.18766 (M^+, +1.29 mDa); Purity by HPLC: 91.8% (254 nm); t_R= 13.1 min (A : B = 50 : 50 → 0 : 100 (20 min); A: 0.1% TFA MilliQ, B: 0.1% TFA CH_3CN).

General Method for Preparation of P-Dots with 1 and Ir Complexes.

P-dots were synthesized by coprecipitation as previously described[22]. A mixture of PVK (15 μL of 2 mg mL^{-1} solution in THF), PEG-COOH (30 μL of 2 mg mL^{-1} solution in THF), **1** (0 or 60 μL of 750 μM solution in THF) and Ir complex **2**–**4** (0 or 60 μL of 750 μM solution in THF) was diluted to 300 μL with THF. The solution was added to 1 mL of MilliQ water on a sonicating bath. The THF was then evaporated in a centrifugal concentrator (MV-100, TOMY) for 2.5 hrs to give 900 μL of P-dots suspension dispersed in MilliQ water. After centrifugation (1000 rpm, 10 min) with MX-105 (TOMY), the supernatant was used as a clear nanoparticle suspension of P-dots doped with **1** and Ir complex.

Fluorescence Detection of NO Release from P-Dots Doped with 1 and 2–4.

An aqueous suspension of P-dots doped with **1** and **2**, **3** or **4** was first diluted 5 times with DPBS containing an NO fluorescence probe, DAF-FM (final 14 μM DAF-FM and 0.2% DMSO)[23], and an aliquot (500 μL) of the diluted suspension was left in the dark for 10 min or irradiated for 10 min at room temperature using a light source (MAX-303) equipped with a 400–430 nm band-pass filter (light intensity: 6.0 mW

cm^{-2} at 420 nm, *n* = 3). Fluorescence intensity was measured with a fluorescence spectrometer, RF5300-PC (Shimadzu), at 515 nm with excitation at 500 nm. Data are expressed as mean + S.E. (shown as error bars; *n* indicates the number of samples). Statistical significance was evaluated by application of a Bonferroni-type multiple *t*-test. ****$p < 0.00001$.

Fluorescence Detection of NO Release from P-Dots Doped with 1 and 3.

An aliquot (500 µL) of the diluted P-dots doped with **1** and **3** in DPBS (14 µM DAF-FM, 0.2% DMSO), the diluted vacant P-dot dissolving 10 µM each of **1** and **3** (14 µM DAF-FM, 0.4% DMSO), and the aqueous solution of 10 µM each of **1** and **3** (14 µM DAF-FM, 0.4% DMSO) were left in the dark for 10 min or irradiated for 10 min with a light source (MAX-303) equipped with a 430–460 nm band-pass filter (light intensity: 40 mW cm^{-2} at 445 nm, *n* = 3) while stirring at room temperature. Fluorescence intensity was measured with a fluorescence spectrometer, RF5300-PC (Shimadzu), and analyzed as described above.

Fluorescence Detection of Photoirradiation-Time-Dependent NO Release from P-Dots Doped with 1 and 3.

An aliquot (700 µL) of the diluted P-dots doped with **1** and **3** in DPBS (7 µM DAF-FM, 0.1% DMSO) was irradiated for 10 min at room temperature 12 times sequentially with a MAX-303 equipped with a 430–460 nm band-pass filter (light intensity: 40 mW cm^{-2} at 445 nm) just after preparation, and at one day after preparation (*n* = 3). Fluorescence intensity was measured after each 10 min irradiation.

Dynamic Light Scattering (DLS) Measurements of P-Dots Doped with 1 and 3.

Aqueous suspensions (1 mL) of P-dots doped with **1** and **3** were diluted with 3 mL of MilliQ water to prepare samples for DLS to determine the distribution of diameter of the P-dots. The measured diameters were expressed as means + S.D.

Preparation of P-Dots Doped with 1 and 3 for ESR measurements.

Aliquots of **1** (0 or 150 µL of 1.5 mM in THF) and **3** (0 or 105 µL of 1.5 mM in THF) were used, and the P-dot suspensions were prepared as described in the section, General Method for Preparation of P-Dots.

ESR measurements of P-Dots Doped with 1 and 3.

A suspension containing 1.03-fold diluted P-dots doped with **1** and **3** was prepared in HEPES buffer (50 mM, pH 7.3) by mixing with a small aliquot containing $FeSO_4 \cdot 7H_2O$ (1.5 mM) and *N*-methylglucamine dithiocarbamate (6 mM) in HEPES buffer solution. The prepared sample suspension was left in the dark or irradiated for 10 min at room temperature with a MAX-303 (band path filter: 430–460 nm, light intensity: 12 mW cm^{-2} at 445 nm) and subjected to ESR studies. ESR spectra were taken on a JES-RE2X spectrometer (JEOL Co. Ltd.). The measurement conditions were as follows: microwave power, 10 mW; frequency, 9.4200 GHz; field, 330 mT; sweep width, 7.5 mT; sweep time, 4 min; modulation width, 0.125 mT; time constant; 0.10 s.

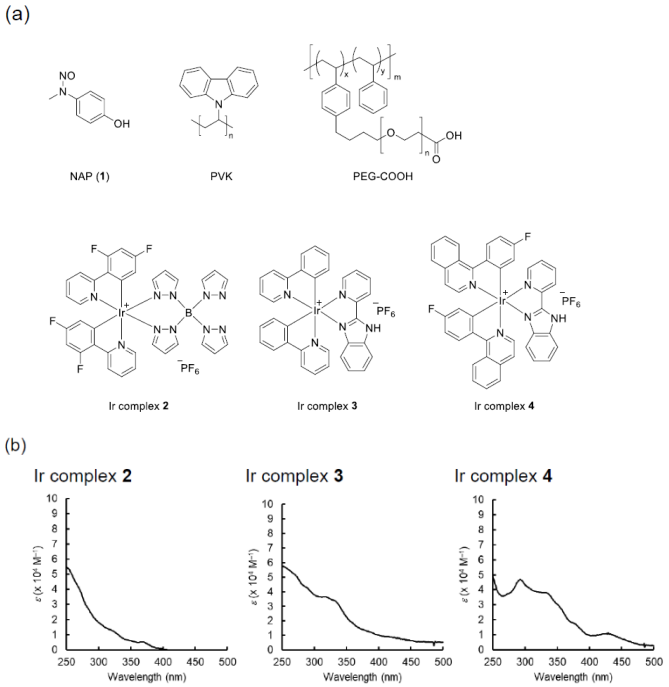


Figure 1. (a) Structures of **1**–**4**, PVK, and PEG-COOH. (b) Measurements of absorption spectra of Ir complexes **2**–**4**. Absorption spectra of a solution of **2**–**4** (10 µM) in THF were recorded.

Results and Discussion

Design and Synthesis.

In order to achieve NO release through intermolecular photoredox reaction, we planned to dope two components, an antenna compound and an NO-releasing compound, into nanoparticles to construct a reaction space in which these components were concentrated. We chose P-dots as nanoparticles because they can be readily synthesized from PVK and PEG-COOH (Fig. 1) and can be easily doped with organic molecules or metal complexes. Cyclometalated iridium (Ir(III)) complexes were selected as antenna dopants because a similar Ir(III) complex has already been doped into P-dots[22], and various groups have reported that Ir complexes work as efficient photoredox catalysts controlled by visible light. Furthermore, their photochemical properties can easily be modulated by changing the ligands (Figure 1a). Ir complex **2** and **3** were prepared by following the previous report[19,20]. Ir complex **4** was prepared in according to Scheme 2. The structure was determined by ^{1}H NMR, ^{13}C NMR, and HRMS. The purity was confirmed by HPLC. Compound **1**, a mimic of the NO-releasing moiety of PeT-based NO releasers that we have previously reported[14], was also doped into the P-dots as the NO-releasing component. The P-dots were prepared by a coprecipitation method as previously described[22]. Briefly, THF solution containing

PEG-COOH, PVK, **1**, and each Ir complex (**2**–**4**) was added to MilliQ water under sonication, and then THF was removed by evaporation under reduced pressure. During the preparation of P-dots, hydrophobic Ir complexes (**2** and **4**) were found to be partially precipitated at the bottom of the centrifuge tube due to their poor solubility in water/THF mixture. In these cases, the supernatant was used as the P-dots solution after centrifugation. The absorption spectra of P-dots doped with **2** and **4** showed a shoulder in the 200–400 nm region, which is similar to that of undoped Ir complex, suggesting low uptake of these Ir complexes into P-dots (Figure S1).

Detection of NO release from Ir-complex-doped P-dots.

First, we examined the photoinduced NO-releasing ability of the prepared P-dots doped with **1**, the NO-releasing component, and **2**, **3** or **4**, the photoredox Ir complex component. The sample solution was irradiated with violet light (400–430 nm, 6.0 mW cm^{-2} at 420 nm, for 10 min), and the released NO was detected by an NO fluorescent probe, DAF-FM. As shown in Figure 2a, a small fluorescence increment was observed in P-dots doped with **1** even in the absence of any Ir complex, whereas no fluorescence increment was observed in the absence of **1**. The small fluorescence increment in the absence of any Ir complex was probably caused by direct photoexcitation and cleavage of the N–N bond of **1** by 400–430 nm light. In the case of P-dots doped with **1** and **3**, photoirradiation induced the largest fluorescence increase (entry ***l*** vs entry ***d***) and the concentration of released NO was calculated to be 1.73 μM, suggesting that **3** is the most suitable dye for this system. It seems likely that complexes other than **3** could not be efficiently doped into the P-dots due to the occurrence of self-aggregation during the concentration process. In the case of **3**, aggregation was not so severe and the complex could be efficiently doped into the nanoparticles. The P-dots doped with **1** and **3** showed an average particle size of about 150–200 nm as measured by a dynamic light scattering method (Figure S2), which is consistent with a previous report. Because **3** showed small but significant absorption at around 430–460 nm (Figure 1b), NO release control by light in this wavelength range was also investigated. As shown in Figure 2b, when the P-dots doped with **1** or **3**, or both of them were irradiated with longer-wavelength blue light (430–460 nm, 40 mW cm^{-2} at 445 nm, for 10 min), a marked fluorescence increment was observed only in the presence of both **1** and **3** (entry ***x*** vs entry ***t***), and the concentration of released NO was calculated to be 4.18 μM. These results suggested that **1** can release NO in the presence of an independent antenna molecule, Ir complex **3**, probably via intermolecular PeT between molecules. When photoirradiation was performed to a mixture of **1**, **3** (10 μM each) and vacant P-dot in DPBS (0.4% DMSO), as shown in Figure 2b, the amount of released NO was higher than in the P-dot doped with **1** and **3** (entry ***y*** vs entry ***x***). As for the smaller amount of NO release in the latter, this result may be caused by the enrichment of concentrated **3** doped inside the P-dot, which suppressed the photoreaction due to the filter effect[24]. The filter effect in this context means high concentrations of dyes interrupt irradiation light to reach the interior dyes, and the efficiency of photoreaction would be decreased. It is also assumed that the less-polar solvent-like environment inside the P-dot suppressed PeT. On the other hand, when a solution of **1** and **3** (10 μM each) without even vacant P-dot in DPBS (0.4% DMSO) was photoirradiated, less NO release was observed than the case of P-dot dopes with **1** and **3** (entry ***z*** vs entry ***y***). These results suggested that **1** and **3** were partially doped with the P-dot when **1**, **3**, and P-dots were mixed separately, resulting in efficient PeT by moderate proximity effect inside the P-dot by avoiding filter effect. Namely, as shown in Figure S3 schematically, in entry ***x***, the strong filter effect among Ir complexes would appear and prevent effective photoexcitation and following PeT. On the other hand, in entry ***y***, the filter effect would be as weak as entry ***z***, while the proximity effect would work between the partially doped **1** (NAP) and Ir complex **3**. Consequently, the condition of entry ***y*** would be most appropriate for effective photoinduced NO release. These differences would give the variation of the amount of released NO. It is noteworthy that DMSO as a co-solvent was necessary for dissolving the compounds into an aqueous solution directly, while a biotoxic co-solvent such as DMSO was not necessary for P-dot doped with the **1** and **3**.

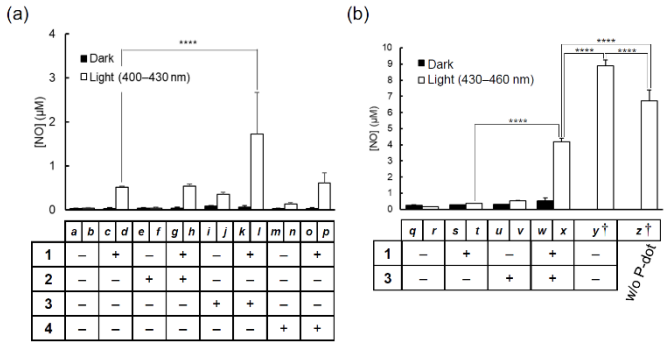


Figure 2. (a) Fluorescence detection of NO release from P-dots doped with **1** and **2**–**4** upon irradiation at 400–430 nm (6.0 mW cm^{-2} for 10 min). (b) Fluorescence detection of NO release from P-dots doped with **1** and **3** upon irradiation at 430–460 nm (40 mW cm^{-2} for 10 min). †**1** and **3** was dissolved in DPBS (10 μM each, 0.4% DMSO).

The stability of the nanoparticles is an important consideration for biological applications. So, we further investigated the stability of P-dots doped with **1** and **3**, which provided the most efficient NO release in response to blue light irradiation. The time course of NO production was evaluated on the same day that the P-dots were prepared and on the following day. As shown in Figure 3a, the amount of NO increased with increasing photoirradiation time and reached a plateau at about 60 min irradiation on the day of preparation, while the NO release the day after preparation was slightly decreased to 75.6% of that on the first day. The particle sizes were also determined by means of dynamic light scattering measurements, and tended to be smaller on the day after preparation in each sample, though the difference was not significant. These results suggest that the prepared P-dots remain functional for at least 24 hours after preparation.

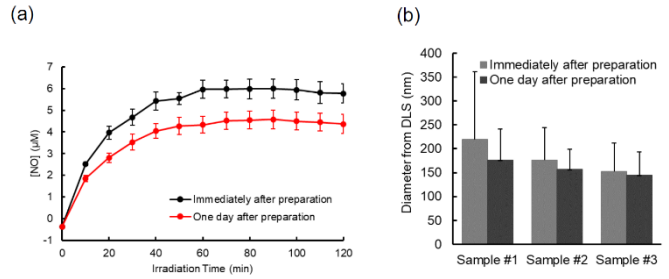


Figure 3. (a) Fluorescence detection of NO release from P-dots doped with **1** and **3** when irradiated for 10 min 12 times sequentially (430–460 nm, 40 mW cm^{-2}) immediately after preparation and one day after preparation. (b) Results of determination of the diameter of P-dots doped with **1** and **3** by means of dynamic light scattering (DLS) analysis immediately after preparation and one day after preparation.

In order to further confirm the photoresponsive NO-releasing ability of P-dots doped with **1** and **3**, ESR spin-trapping studies using iron ion with *N*-methylglucamine dithiocarbamate (Fe-MGD) were carried out (Figure 4). Fe-MGD efficiently traps NO and forms a NO-Fe-MGD complex, which shows a typical three-line signal at around 330 mT in 1 GHz ESR spectrometry. We also measured the ESR spectra in the presence of an Mn^{2+} marker as an internal standard (Figure S4). After photoirradiation (430–460 nm, 12 mW cm^{-2} at 445 nm, for 10 min), ESR measurements showed a significant NO-Fe-MGD signal in P-dots doped with **1** and **3**. A small triplet signal was also observed in the absence of **3**. This result is consistent with the finding that slight fluorescence was observed even in the absence of any Ir complex (Figure 2). In the absence of **1**, the triplet signal was hardly observed. These results support the idea that P-dots doped with **1** and **3** work as an efficient photoresponsive NO releaser, as expected. These results can be explained in terms of efficient intermolecular PeT between **1** and Ir complex **3** followed by efficient NO release via a long-lived triplet excited state upon photoirradiation, as shown in Scheme 3[25].

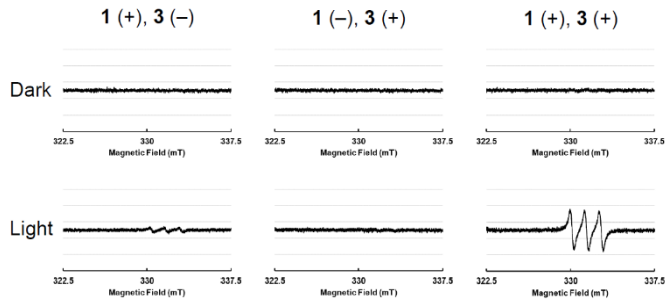


Figure 4. ESR measurements. A suspension containing P-dots doped with **1** and **3**, $FeSO_4{\cdot}7H_2O$ (1.5 mM), and *N*-methylglucamine dithiocarbamate (6 mM) in HEPES was irradiated at 430–460 nm (12 mW cm^{-2} for 10 min).

Conclusions

Polymer nanoparticles, P-dots doped with Ir complex **3** together with *N*-methyl-*N*-nitroso-4-aminophenol (**1**) are easily prepared and show efficient visible-light-responsive NO-releasing ability. The mechanism of NO release is proposed to involve intermolecular PeT via the triplet excited state of the dye. The advantage of intermolecular PeT is that the dyes can be easily replaced, resulting in efficient screening of many candidate dyes. These nanoparticles did not require biotoxic co-solvents to dissolve metal complexes or organic compounds. Since it was reported that a P-dots of similar composition was applied *in cellulo* without remarkable toxicity[22], and the other one could release NO via photo-thermal pathway to show antibacterial effect[26], our P-dots are expected to be useful tools for investigating the mechanisms of the diverse biological effects of NO.

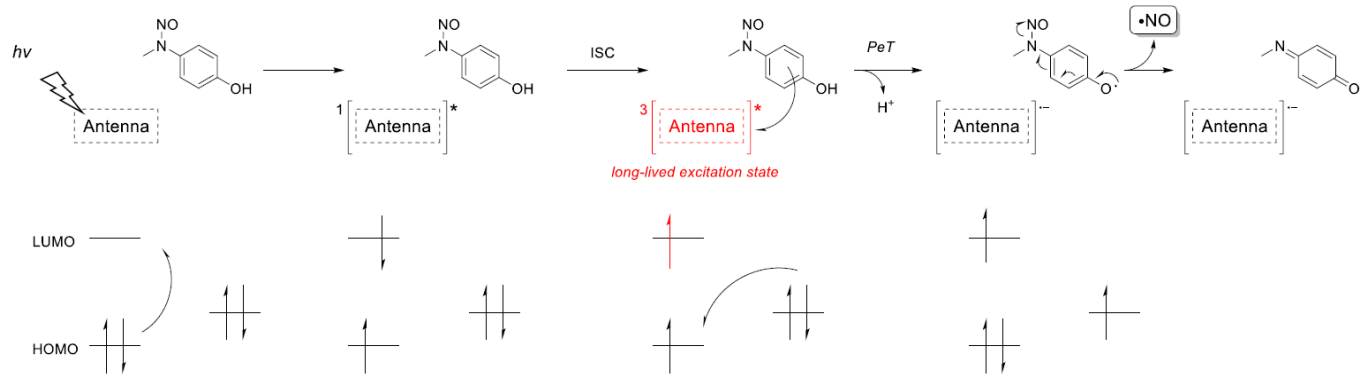
Author Contributions

D.S., A.S. and N.I. contributed to the study conceptualization. Z.L., Y.O. and M.F. contributed to synthesize the compounds. D.S. contributed to the analysis and drafted the manuscript. M.K. and H.N. supervised the conduct this study. All authors approved the final version of the manuscript for submission.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements



Scheme 3. Proposed mechanism of intermolecular PeT via a triplet excited state.

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