Conjugated polymers as molecular gates for light-controlled release of gold nanoparticles

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ABSTRACT

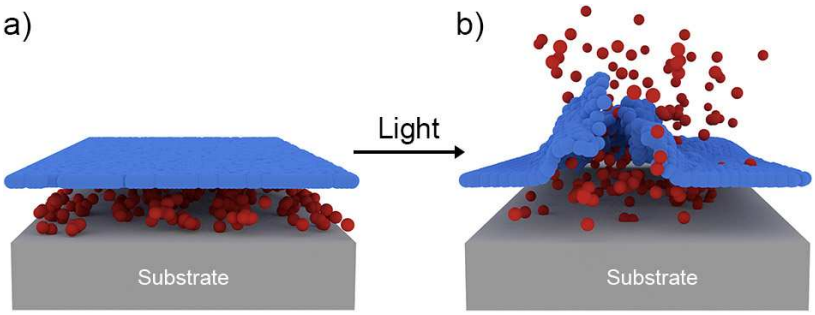
The remote release of nano-objects from a container is a promising approach to transduce chemical events into an optical signal. The major challenge in the development of such a system involves the use of a suitable molecular gate that retains aggregated particles and releases them upon applying an external stimulus. We show proof-of-concept experiments for the release of gold nanoparticles into an aqueous solution upon photodegradation of conjugated polymer thin films. Gold nanoparticles thus transduce light-induced chemical events into an amplified optical signal with a release rate of 2.5 nM per hour, which can be readily detected by the naked eye.

KEYWORDS Photodegradation, Remote release, Signal amplification, Reversible self-assembly, Gold nanoparticles

The release of cargo from a container is a core concept behind chemical signal amplification in living systems.[1] For instance, an individual hormone molecule interacting with a membrane receptor invokes multiple chemical processes in the cell interior, an efficient strategy to maximize redundancy in signaling and to eliminate error propagation. Similarly, signal amplification by the controlled release of nano-objects is a promising approach to mimic natural systems.[2] In this context, metal nanoparticles can transduce (bio)chemical events into an optical signal, thereby allowing (bio)sensing.[3] In a recent example, Grzybowski and co-workers reported the release of gold nanoparticles from micron-sized supercrystals by enzymatic digestion of a molecular shell acting as a gate.[4] Such nanoparticle-based signal amplification strategies are promising toward novel sensing strategies with simple practical implementation. The release of nanoparticles from a confined space is obviously a nontrivial task, requiring a judicious choice of chemical tools that make feasible the following steps: aggregation of nanoparticles, closing the molecular gate, and subsequently releasing the cargo. The major difficulty relies on the proper design of a molecular shell that is expected to retain the aggregated particles and release them only upon application of an external stimulus, such as light.

Owing to their outstanding optical properties, conjugated polymers are used in a number of light-related applications such as photovoltaics,[5] photodynamic therapy[6] or photocatalysis.[7] Although the polymers can be processed in liquid phase into a wide variety of functional forms (*e.g.* colloids, printable thin films), their degradation in the presence of light and/or oxygen is a drawback that requires novel synthetic approaches for improvement of their structural stability.[8] Interestingly, the structural instability of conjugated polymers can be seen as an advantage if the polymer is to be used as a photosensitive 'gate' to remotely release the nano-cargo into solution.

Our central hypothesis is described in Scheme 1: a conjugated polymer thin film covers gold nanoparticle aggregates, preventing their dispersion in water. Under light irradiation the thin film degrades, allowing nanoparticle release that is detectable by the naked eye. Therefore, the nanoparticles act as a signal transducer via amplification of structural and chemical changes in the polymer film.



Scheme 1. a) A thin polymer film (blue) prevents redispersion of gold nanoparticles (red) from a solid substrate (grey) into an aqueous solution. b) Visible light irradiation degrades the polymer releasing the nanoparticles into solution.

To evaluate our hypothesis, the nanoparticles acting as signal transducer need to remain aggregated in chloroform, (good solvent for the polymer) and get redispersed in water (bad solvent for polymer) with no need for stirring, shaking or sonication. We prepared reversible aggregates of gold nanoparticles by modification of a reported method,[9] in which the combination of two solutions of oppositely charged nanoparticles leads to the formation of aggregates at a specific pH. To ensure negative surface charge (-44.1 mV) at high pH, initially hydrophobic gold nanoparticles[10] (4.9 ± 0.9 nm) were functionalized with mercaptoundecanoic acid (MUA). On another batch, functionalization of the nanoparticles with 11-mercaptotetramethylammonium salt provided a positive surface charge of +18.1 mV (Figure S1).

In a typical aggregation process, the negatively charged nanoparticles (AuMUA) were mixed with positively charged nanoparticles (AuTMA) at pH 12, leading to phase separation, as reflected in a color change from reddish to violet. The aggregates were washed by centrifugation and resuspended in an aprotic polar solvent, such as acetonitrile (Figure 1a,c). Transfer of the aggregates into pure water led to immediate redispersion of the particles. Importantly, the nanoparticles in aggregated state can also be transferred onto a glass substrate and dried, but once immersed in pure water the nanoparticles diffuse into the solvent causing the coloration (Figure 1b,d). Such a spontaneous redispersion is crucial for our purpose, since the aggregates can be safely stored as a dry powder.

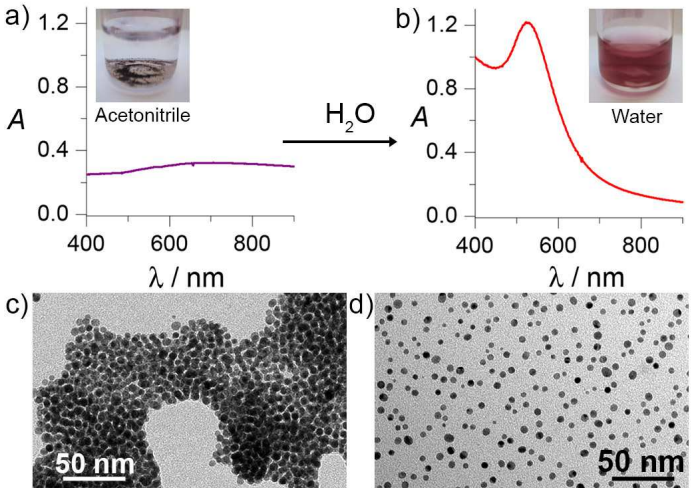


Figure 1. Reversible aggregation of gold nanoparticles. UV-Vis spectrum (a) and TEM image (c) of aggregates formed by mixing oppositely charged nanoparticles, which remain aggregated in acetonitrile. UV-Vis spectrum (b) and TEM image (d) of nanoparticles redispersed in water.

We used two different polymers, namely poly-Th-DPP[11] (Figure 2a – see SI for experimental details) and commercially available regiorandom-P3HT (Figure 2b). Both polymers formed thin films with a thickness of ~200 nm when spin-coated on the glass substrate (Figure 2e). UV-Vis

spectroscopy provided valuable information on the optical features of the polymers, both in solution (chloroform), and as thin films (Figure 2c,d). In the case of poly-Th-DPP, the presence of two broad absorption bands at 380 and 614 nm suggested a high degree of conjugation between the donor and acceptor units within the rigid polymer chain. The intramolecular charge transfer between the thiophene and diketopyrrolopyrrole (DPP) segments originates the main absorption band at 614 nm (in solution), which shifted to 657 nm after spin-coating. The shift suggests an increased probability of low energy transitions due to long range ordering of aromatic molecules in the solid state,[12] facilitated by strong π-π stacking interactions between the planar DPP skeletons of neighboring molecules.[13] We observed a similar optical behavior for the P3HT polymer, in which the maximum of the absorption band shifted from 428 nm in solution to 441 nm after spin-coating, again due to an increased degree of order in the solid polymer.

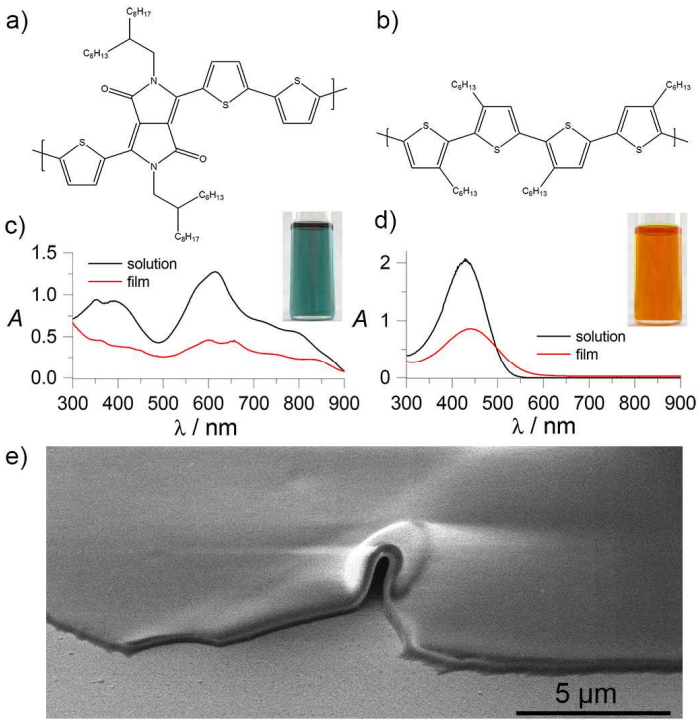


Figure 2. Chemical structure and UV-Vis spectra of (a, c) poly-Th-DPP and (b, d) P3HT polymers in chloroform solution (black lines) and as thin films on glass slides (red lines). (e) Representative SEM image of a poly-Th-DPP polymer film with a thickness of ~200 nm.

To study film degradation we immersed the glass substrates (1 cm^2) covered with polymer films (P3HT or poly-Th-DPP) in quartz cuvettes filled with 1 mL of water and irradiated perpendicularly with white light (350 – 1100 nm, 150 mW/cm^2) for 2 hours at 40 ºC. Exposure of the substrate to light led to a gradual decay of the optical absorption, whereas no changes were observed if stored in the dark. The effect of irradiation could be readily observed by eye, indicating physical changes in the film (Figure 3).

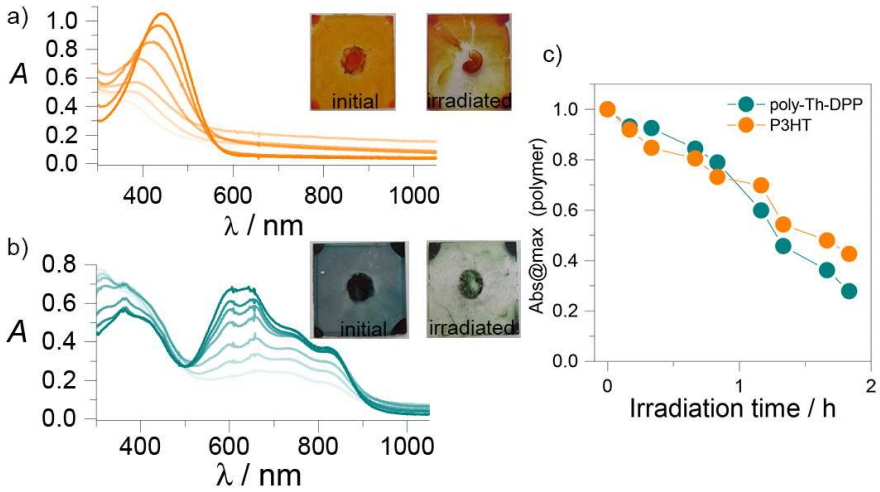


Figure 3. Photodegradation of polymer films. (a,b) Time-dependent UV-Vis monitoring of P3HT (a) and poly-Th-DPP (b) films under irradiation with visible light. Inset: photographs of the films before and after irradiation. c) Variation of maximum absorbance with irradiation time, showing a similar degradation rate for both polymers.

For P3HT, the absorption maximum at 440 nm showed a linear decay accompanied by a blueshift of ~65 nm (Figure 3a),[14] which originated from the reduction of the π-conjugation length caused by the breakage of double bonds in the thiophene units.[15] Detailed MALDI-TOF-MS characterization of P3HT films before and after irradiation confirmed the fragmentation of the polymer into smaller subunits (Figure S2), as recently reported.[16] In the case of poly-Th-DPP, the irradiation led to absorption damping at longer wavelengths (> 500 nm), without blueshift (Figure 3b). We postulate that the DPP units are more susceptible to the attack by reactive oxygen species than thiophene units, which could lead to the opening of double 5-member rings. Progressive degradation of DPP units prevents intramolecular charge transfer from thiophene to DPP, which explains damping of the band without noticeable blueshift. This hypothesis was confirmed by MALDI-TOF MS analysis, which showed absence of polymer fragmentation after irradiation (Figure S3). This behavior was expected since DPP-based materials exhibit excellent chemical stability.[17] Raman scattering spectroscopy further confirmed the degradation of the polymer films (Figure S4). For P3HT, the characteristic peaks (721 and 1454 cm^{-1}) disappeared completely while the Raman spectrum of the poly-Th-DPP film remained unchanged after irradiation.

We used the spin-coating technique to cover the aggregates with polymer films and found that mechanical pressing of the relatively large aggregates (>1 μm) was crucial, prior to spin coating, to avoid the leakage of the nanoparticle into the solution beneath the polymer thin film of ~200 nm (see Figure S5 for SEM analysis of the partially covered aggregates). On the other hand, if the polymer was drop-casted from a chloroform onto the aggregates, thicker films were formed that prevented nanoparticle release, even under prolonged irradiation (Figure S6).

Irradiation of the polymer film on the aggregates led to the remote release of nanoparticles into water, as observed by the naked eye (Figure 4a inset). Time-dependent monitoring of the solution showed a gradual increase of a localized surface plasmon resonance band, in agreement with an increased Au nanoparticle concentration in solution (see Figure 4a for poly-Th-DD and Figure S7 for P3HT). We estimated the release rate of the nanoparticles by recording the absorbance at 400 nm, which can be translated into the number of the particles per unit volume.[18] The faster release rates of 2.6 nM per hour for poly-Th-DPP, as compared to 0.75 nM per hour for P3HT (Figure 4b), was rather surprising especially considering that the degradation rate is similar for both polymers (Figure 3c). This is likely due to a higher absorption of the light emitted from the halogen lamp[a] by the green-colored poly-Th-DPP, as compared to P3HT. We exclude the possibility of a thermal effect caused by plasmon heating since poly-Th-DPP absorbs efficiently in the visible, thereby inhibiting absorption by the aggregated nanoparticles. Additionally, the plasmon-heating effect would involve power densities of incoming light in the order of W per cm^2. We used white light with a power density of ~150 mW/cm^2, which is too low to induce plasmon heating. Relatively strong light absorption by the polymer and the lack of chemical changes in the poly-Th-DPP film suggests mechanical deformation of the film. Although the local temperature during irradiation is hard to estimate, it is suggested that a local phase transition can facilitate mechanical changes in the film. Careful inspection of the films by SEM analysis showed that the initially smooth films (Figure 4c and S8) became porous, with multiple cracks and hollow spaces (Figures 4d and S9), facilitating the release of the particles. On the other hand, photodegradation of P3HT is dominated by chemical processes – as observed by UV-Vis, Raman, MALDI -, which lead to formation of intermediate radicals that can affect the stability of the nanoparticles and hinder their release. SEM analysis revealed the presence of

remaining particles beneath the irradiated P3HT film, which was not the case for Poly-Th-DPP (for comparison see Figure S9 c and f).

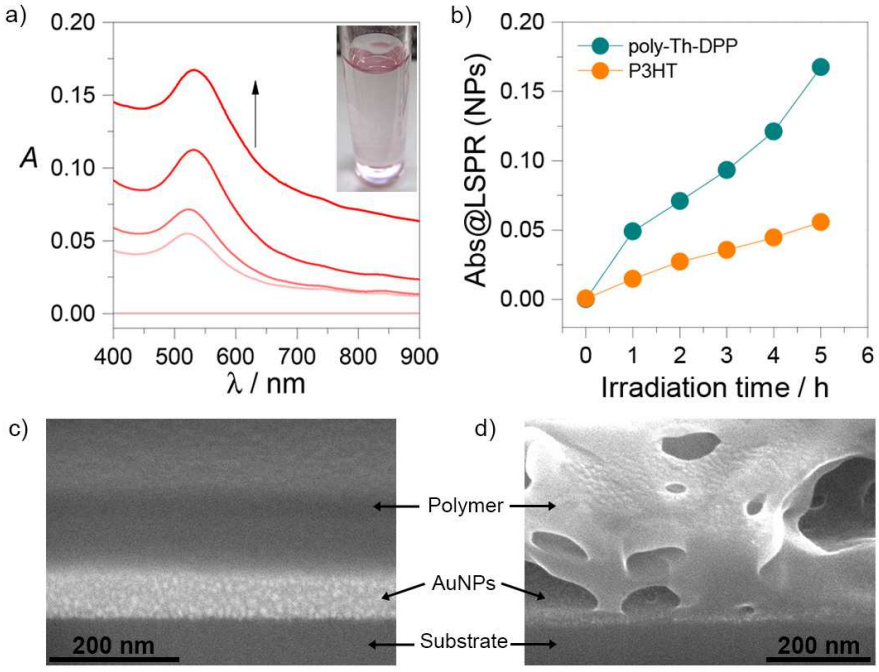


Figure 4. Nanoparticle release under irradiation. (a) Time-dependent UV-Vis spectra of the solution with gradually increasing concentration of nanoparticles. Inset: photograph of the solution containing released particles. (b) Time-dependent absorbance changes of the gold nanoparticle solution during irradiation, showing faster release for the poly-Th-DPP film. (c,d) SEM images of the P3HT film (cross-section) before (c) and after (d) irradiation.

In summary, we demonstrated proof-of-concept experiments for the remote release of nanoparticles into aqueous solution by photodegradation of a thin polymer film that acted as a molecular gate. We concluded that the release of nanoparticles was faster when using a polymer that absorbs a wider spectral range matching the features of the incident light. Although the observed release rate is still slow, there is room for improvement by optimization of parameters such as film thickness, particle size or irradiation intensity. However, since the particles release

can be readily monitored by eye, we expect that our approach will open up new possibilities in the field of sensing. For example, functionalization of the polymer with receptor molecules could hinder (or boost) molecular gate opening in the presence of light, which could lead to the emergence of an optical signal induced by a recognition process at the molecular level.

ASSOCIATED CONTENT

Supporting Information. Experimental details, UV-Vis spectra, Raman and SEM analysis of the initial nanoparticles and films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

[a)] For the spectral profile of the lamp used in all experiments see Figure S7.

The authors declare no competing financial interests.

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