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## ARTICLE

## Fabrication of single-chain nanoparticles through the dimerization of pendant anthracene groups via photochemical upconversion

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We report on the use of visible light as the driving force for the intramolecular dimerization of pendant anthracene groups on a methacrylic polymer to induce the formation of single-chain nanoparticles (SCNPs). Using a 532 nm green laser light source and platinum octaethylporphyrin as a sensitizer, we first demonstrated the use of TTA-UC to dimerize monomeric anthracene, and subsequently applied this concept to dilute poly((methyl methacrylate)-*stat*-(anthracenyl methacrylate)) samples. A combination of triple-detection size-exclusion chromatography, atomic force microscopy, and UV-visible spectroscopy confirmed the formation of the SCNPs. This report pioneers the use of TTA-UC to drive photochemical reactions in polymeric systems, and showcases the potential for TTA-UC in the development of nanoobjects.

### 1. Introduction

The interest in photochemical upconversion, also referred to as triplet-triplet annihilation upconversion (TTA-UC) has been rising in the past decade.<sup>1–3</sup> While upconversion is basically a method to convert low energy photons into higher energy light, the ability to use simple light sources (non-coherent and low power density) gives TTA-UC an advantage compared to other upconversion methods, such as second-harmonic generation and multi-step excitation of lanthanides.<sup>4,5</sup> Since its first demonstration by Parker and Hatchard in 1962,<sup>1,6</sup> most of the intricacies behind TTA-UC have been explained. First, the sensitizer absorbs the incident light and is excited to its singlet state. This singlet excited state is then converted to a triplet via intersystem crossing, before population of the emitter triplet levels via a Dexter-type energy transfer from the sensitizer. The collision of two triplet emitters, otherwise referred to as triplet-triplet annihilation (TTA), leads to the formation of the singlet excited state of one emitter and its subsequent decay is responsible for the upconverted fluorescence.<sup>7</sup> TTA-UC has found use in a wide variety of fields, including harnessing low-energy light beyond the visible range in solar harvesting,<sup>8</sup> or taking advantage of the anti-Stokes shift to minimize the background autofluorescence of tissues in bioimaging.<sup>9</sup> However, photochemical reactions based on TTA-UC have been relatively limited. The ability to use low energy light is often desirable in cases where high-energy irradiation is undesirable

(e.g. biological samples). Of particular interest to this work is the report by Isangulov et al. who demonstrated the [4+4] cycloaddition dimerization of anthracene using sensitized upconversion.<sup>10</sup> This dimerization process, which otherwise requires light in the UV region,<sup>11</sup> proceeded using upconverted energy from the selective excitation at 458 nm of metal-to-ligand charge transfer (MLCT) band of [Ru(dmb)3]<sup>2+</sup> (dmb=4,4'-dimethyl-2,2'-bipyridine).<sup>10</sup>

Also of interest is the emerging field of single-chain nanoparticles (SCNPs), which are structurally defined nanoparticles formed by the collapse of polymer chains via intramolecular crosslinking. SCNPs are thought to bear promise in a variety of areas including catalysis,<sup>12</sup> nanomedicine,<sup>13</sup> and chemical sensors.<sup>14</sup> They draw inspiration from the three-dimensional architecture of proteins, whose functionality is often the result of sequence control of their constitutive building blocks (i.e. amino acids).<sup>15</sup> In nature, folding is achieved through secondary bonding (covalent or not), such as hydrogen bonding or disulfide bridges.<sup>16</sup> With the view to emulate these structures, several synthetic strategies have been implemented, such as metal ligation,<sup>12</sup> Friedel-Crafts alkylation,<sup>17</sup> disulfide-formation,<sup>18</sup> and a range of 'click' chemistry reactions.<sup>19</sup> Several groups in the field have worked to greatly further knowledge about SCNPs and their usefulness.<sup>8,15,20–22</sup> Recently, Frank et al. demonstrated a straightforward method of producing SCNPs by dimerizing pendant anthracene units dispersed along a methacrylic chain.<sup>23</sup> Upon irradiation of these polymer chains with high energy UV light in dilute solutions, [4+4] cycloaddition of pendant anthracene groups occurred, producing SCNPs. Of the available anthracene groups, up to 88% took part in the dimerization process. This report, combined with the aforementioned work of Isangulov et al. on TTA-UC dimerization of anthracene,<sup>10</sup> provides an opportunity to achieve the synthesis of SCNPs using low-energy irradiation.

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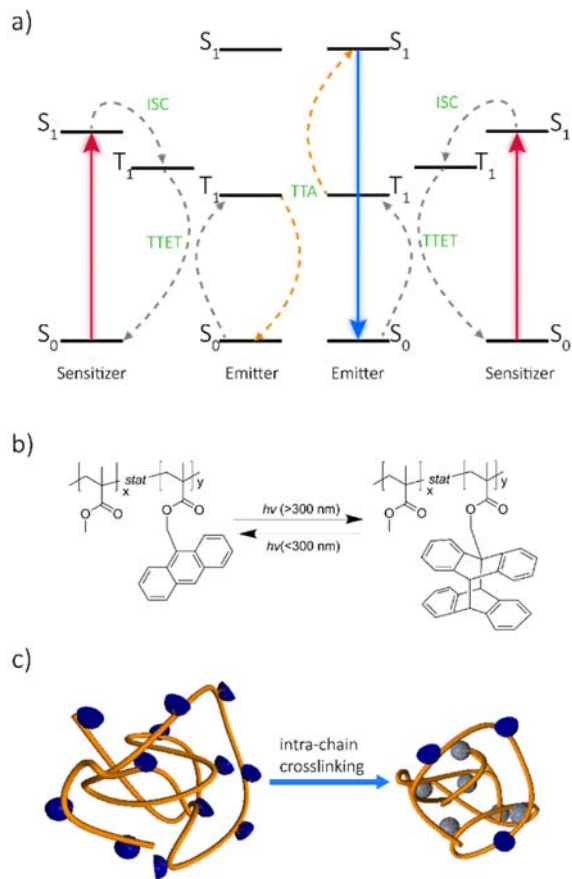
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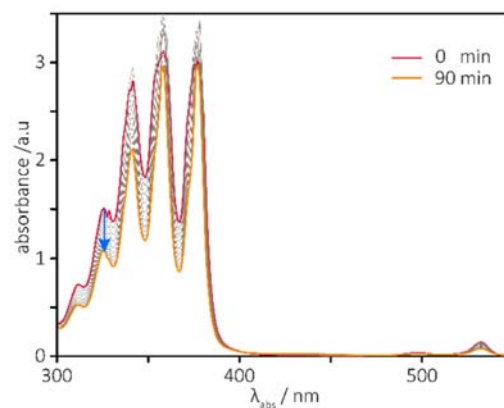
**Fig. 1:** (a) A schematic representation of the mechanism for triplet-triplet annihilation upconversion. In this case, PtOEP serves as the sensitizer while the emitted energy drives the anthracene dimerization. (b) (top) Schematic representation of the [4+4] cycloaddition dimerization of anthracene powered by UV energy. (bottom) Schematic illustration of the collapse in the formation of SCNPs induced by the intra-chain crosslinking. Blue half-spheres represent anthracene while gray spheres represent photodimers

Herein, we report the use of TTA-UC to drive the dimerization of pendant anthracene chains in the synthesis of SCNPs. Using 532 nm light, we first demonstrate the TTA-UC in the dimerization of monomeric anthracene using a platinum octaethyl porphyrin (PtOEP) sensitizer, before successfully applying the same principle to polymeric systems. Various polymeric systems have been used in photochemical upconversion.<sup>3,24</sup> However, to the best of our knowledge, this is the first use of TTA-UC to drive photochemical reactions in a polymeric system but more importantly for the fabrication of nano-objects.

## 2. Results and discussion

### 2.1. Demonstration of feasibility of dimerization of anthracene using PtOEP

To demonstrate anthracene dimerization via TTA-UC, Isangulov and Castellano used a 458 nm laser light source to excite the

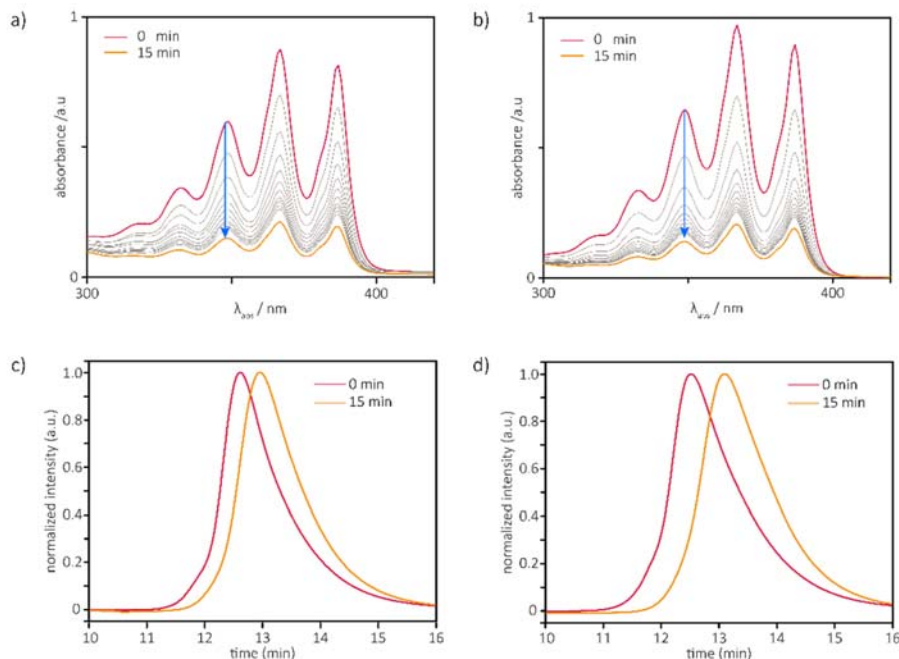


**Fig. 2:** UV-vis absorbance spectrum of a solution of anthracene and PtOEP in acetonitrile irradiated with 532 nm light. The absorbance was shown to decrease upon irradiation, suggesting that anthracene dimerization was taking place.

[Ru(dmb)3]<sup>2+</sup> sensitizer.<sup>10</sup> Taking advantage of its Q absorption band (536 nm), we chose PtOEP as the sensitizer. The latter was excited using a low-power continuous solid-state 532 nm laser as the light source (maximum 10 mW).<sup>25</sup> We first tested if anthracene dimerization could be successfully performed under these conditions. Charlton et al. demonstrated that under oxygen-free conditions, the dimerization of anthracene proceeded by TTA.<sup>11</sup> High monomer concentration and oxygen are detrimental to this process. As demonstrated by Isangulov et al., dimerization leads to the consumption of the anthracene monomer. In turn, this conversion to the dimer form results in a decrease of the characteristic absorbance bands in the 300–400 nm region of the spectrum. The formation of endoperoxides would also lead to a decrease in this absorbance, hence the need to thoroughly degas the solutions.

The absorbance spectrum of the PtOEP sensitizer also shows a maximum at 384 nm, attributed to the Soret band of the octaethylporphyrin ring.<sup>25</sup> While maximum upconversion was reportedly achieved at higher anthracene concentrations with respect to PtOEP sensitizer,<sup>7</sup> it was necessary here to lower the concentration of the sensitizer to easily visualize the evolution of anthracene peaks. An anthracene concentration of  $7.29 \times 10^{-5}$  M in acetonitrile was chosen. After multiple trials (data not shown), a concentration of  $1.7 \times 10^{-5}$  M for the PtOEP was finally chosen as a good compromise to monitor the change in absorbance. UV-vis spectra were taken at 10 minute intervals of irradiation. As anticipated, the decrease of the anthracene bands (Fig. 2) suggests that the dimerization is happening. Furthermore, photodimer solid particles precipitated over the course of the reaction, as previously demonstrated.<sup>10</sup> This precipitate was confirmed by <sup>1</sup>H-NMR spectroscopy (Fig. S1, ESI); the new peak at 4.5 ppm, characteristic of the bridgehead methine peaks in the anthracene dimer, was observed<sup>26</sup> concomitantly with an upfield shift in the aromatic peaks.

### 2.2. Fabrication of SCNPs under UV irradiation



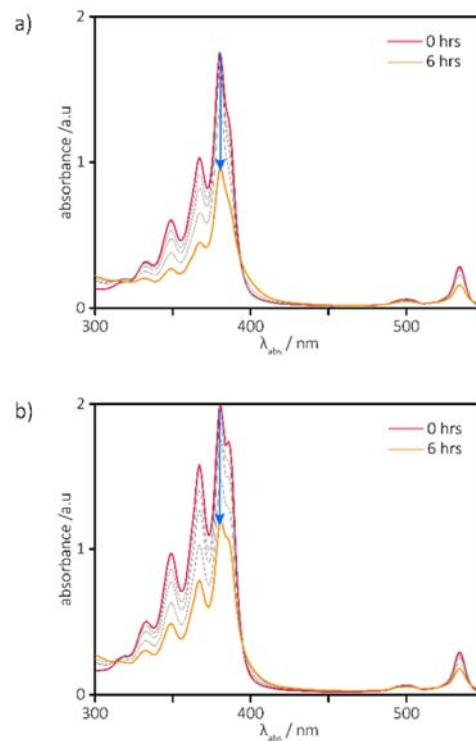
**Fig. 3.** The UV-vis absorbance spectra for (c) **P1** and (d) **P2** at indicated time intervals. Both samples show a decrease in absorbance, supporting that dimerization occurred. Changes in the retention times for polymer samples before (red) and after (blue) irradiation with UV light for (a) **P1** and (b) **P2**. Both plots used data from the UV detector.

Prior to demonstrating PtOEP sensitization strategies to polymeric samples, we attempted to reproduce the fabrication of SCNPs by UV irradiation. To that end, statistical copolymers of methyl methacrylate (MMA) and the 9-anthracenylmethyl methacrylate (AnMA) were synthesized via reversible addition chain-transfer (RAFT) polymerization.<sup>7</sup> Two polymers with different compositions were used; **P1**, which contained 10% AnMA (Fig. S2, ESI) and **P2**, which contained 20% AnMA (Fig. S3, ESI). As expected, when exposed to 366 nm UV light, a decrease in absorbance was observed, suggesting that the UV light was inducing the dimerization of pendant anthracene groups. Dilute solutions of polymers (0.1 mg/mL) were used to limit interchain dimerization.<sup>23</sup> Moreover, size-exclusion chromatograms also showed a clear increase in retention times, characteristic of a contraction of the hydrodynamic volume as the polymers transitioned from random coils to more compact, collapsed structures (Fig. 3b).<sup>12</sup> When the samples were irradiated with 254 nm light, less than 40% of the intensity of the original anthracene bands (prior to any irradiation) was recovered, showing incomplete cycloreversion consistent with the findings of Frank et al. (Fig. S4, ESI).<sup>23</sup>

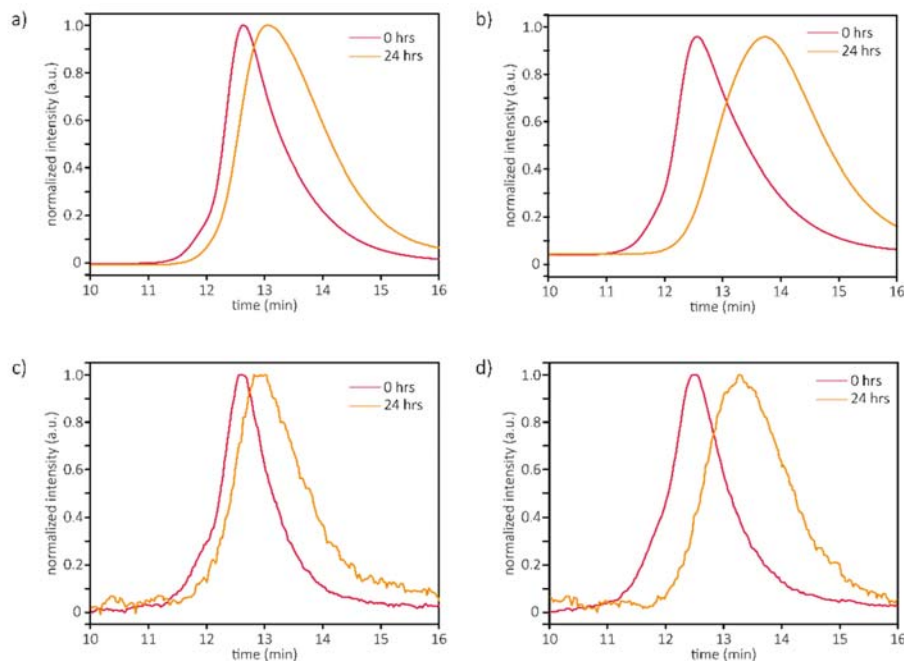
### 2.3. Fabrication of SCNPs by TTA-UC

Combining PtOEP-sensitized dimerization and UV-triggered SCNP formation with **P1** and **P2**, we then set out to induce SCNP fabrication using visible light. Again, the concentration of the PtOEP sensitizer (0.01 mg/mL and 0.0125 mg/mL for **P1** and **P2** respectively) was reduced to facilitate the visualization of the anthracene band decrease while allowing the reaction to proceed (Fig. 4 and Fig. S5, ESI). Upon irradiation with a 532 nm

laser, the aforementioned decrease in absorbance of the vibronic signature between 300 and 400 nm was observed.



**Fig. 4.** The UV-vis absorbance spectra for (a) **P1** and (b) **P2** at indicated time intervals. Both samples show a decrease in absorbance, supporting that dimerization occurred in the formation of SCNPs.



**Fig. 5.** Changes in the retention times for polymer samples (a) **P1** and (b) **P2** before (red) and after (blue) irradiation with 532 nm light for 24 hours from the UV detector. The retention times for polymer samples (c) **P1** and (d) **P2** before (red) and after (blue) irradiation with 532 nm light for 24 hours from the LS detector.

While the 536 nm band characteristic of PtOEP remained unchanged at early reaction times (< 3h), a decrease in the Q band was observed as the irradiation continued. We attribute this decrease to the degradation of the PtOEP. Interestingly, control experiments without any polymer do not display this decrease in absorbance (Fig. S6, ESI), which is indicative of the active role of the polymer in the degradation of the sensitizer, possibly due to the presence of chain-transfer agents.<sup>27</sup>

The SEC results also confirmed an increase in the retention time, consistent with polymers of lower hydrodynamic radius. The shift was slightly more pronounced for **P2**, likely because of the higher anthracene content. For both **P1** and **P2**, no noticeable high-molecular-weight shoulder appeared, confirming again the absence of significant interchain dimerization at these low concentrations. Blasco et al. pointed that a common error in the demonstration of the formation of SCNPs was the utilization of calibration standards in SEC.<sup>28</sup> This relative method often does not account for compositional changes and their resulting influence on solvodynamic properties compared to standards, such as polystyrene and poly(methyl methacrylate) (PMMA). Here, a direct comparison to PMMA standards is facilitated by the methacrylic nature of **P1** and **P2** polymers. Moreover, this shift was observed on all three detectors (UV, dRI and LS) of the SEC instrument thereby demonstrating that the polymer chains had indeed collapsed into SCNPs.

To confirm the need for metal sensitization in the formation of SCNPs, polymer solutions at identical concentrations were also irradiated in the absence of PtOEP for up to 6 hours. No significant changes in absorbance were detected upon

irradiation, confirming the role of the metal sensitizer in the dimerization (Fig. S7, ESI).

The particles were also visualized using atomic force microscopy (AFM) on a mica surface and individual particles were clearly identifiable. SCNPs from **P1** at 0.1 mg/mL showed small individual particles with diameters of ca. 20 nm and a few aggregates, some as big as 400 nm, presumably as a result of the deposition method. The height profile in AFM suggests that the aggregated particles had heights of up to 30 nm, while the majority of the nanoparticles were below 20 nm.

In contrast, SCNPs from **P2** appeared to form fewer aggregates. The lack of clustering may be attributed to technique during sample preparation during deposition.<sup>29</sup> The largest observed nanoparticles had diameters of up to 170 nm, compared to the 400 nm observed in the **P1** sample. The height profiles also suggest more compact structures, with the highest values around 25 nm, and the average heights around 10 nm. These results hint at greater collapse in samples with the higher anthracene concentrations.

### 3. Conclusions

We have successfully demonstrated the use of TTA-UC as a novel synthetic tool for the formation of SCNPs and more generally to fabricate new nano-objects. This report opens up new possibilities to use TTA-UC to perform chemistry with polymers in situations where UV light is not desirable (e.g. nanomedicine, deep tissue penetration). The ability to control nano-object formation by placing metal sensitizers at specific locations to control crosslinking is also quite appealing. To

achieve this, more studies will be done to determine precisely the minimum local concentration of sensitizer necessary to achieve acceptable levels of dimerization. These metal-containing units (e.g. Pd complexes) may also expand beyond

the sensitization role, and play a role in areas such as (photo)catalysis or chemical sensing. Light responsiveness is now a highly sought-after property in the development of smart

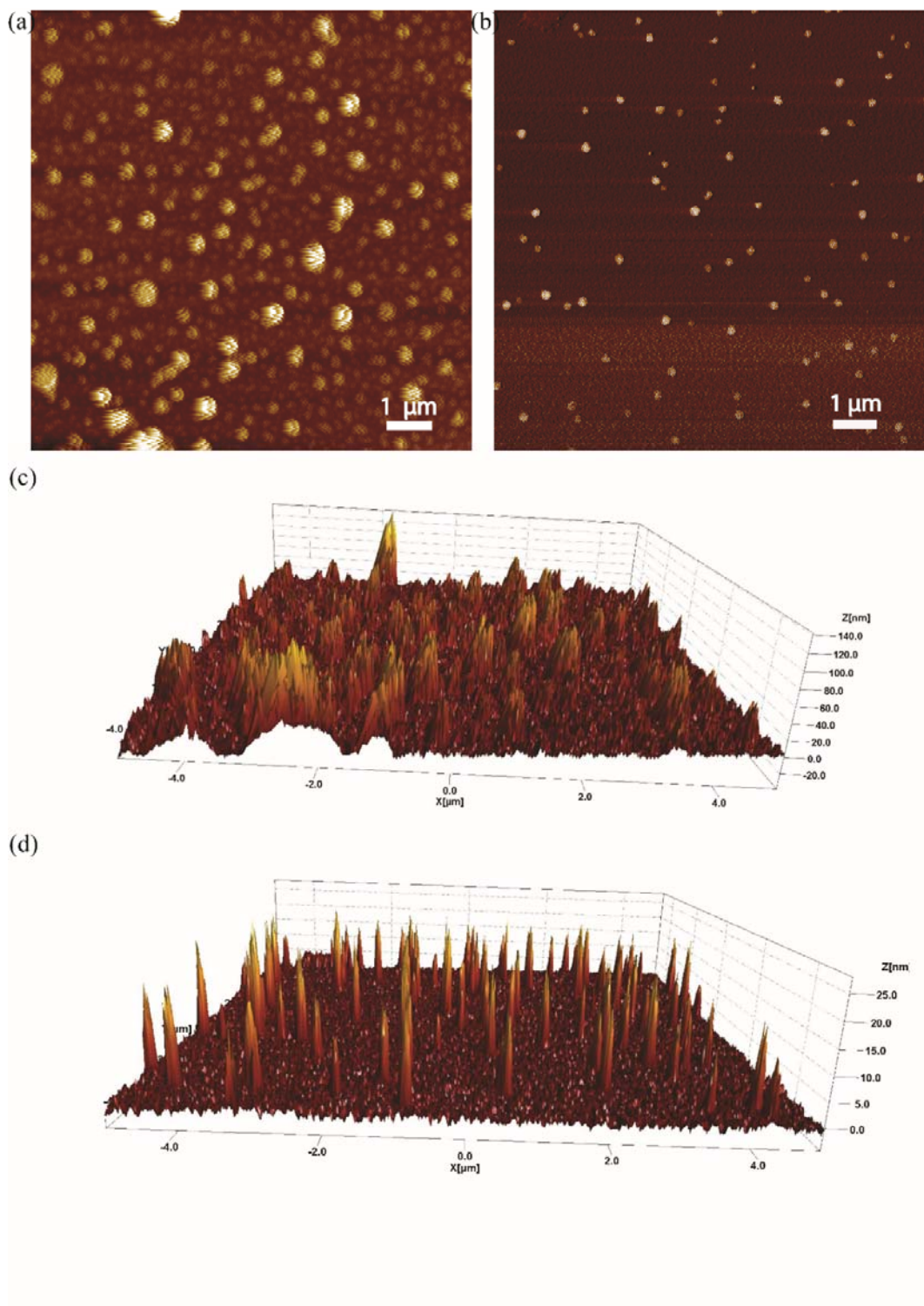


Fig. 6. AFM images of SCNPs on a mica surface. (a) Images of sample P1 and (b) sample P2. The 3-D height profiles of (c) P1 and (d) P2.

materials,<sup>30</sup> and this manuscript alludes to the potential value of TTA-UC in this field.

## 4. Experimental

### 4.1. Materials

PtOEP (Frontier Scientific, Logan, Utah, USA), anthracene (Sigma Aldrich), methacrylic acid (Sigma Aldrich), Anthracen-9-ylmethanol (Sigma Aldrich), 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB) (Sigma Aldrich), acetonitrile (Fisher Scientific) were used as purchased. Methyl methacrylate (Sigma Aldrich) was filtered through basic alumina to remove inhibitor before used. Tetrahydrofuran (THF) and *N,N*, dimethylformamide (DMF), purchased from Fisher Scientific were used directly from a solvent purification system (PureSolv MD 5, INERT Technology). Anthracene methacrylate (AnMA) was synthesized using a previously published method.<sup>31</sup>

### 4.2. Synthetic procedures

**Synthesis of poly(methyl methacrylate)-stat-Anthracenyl methacrylate (pAnMA-stat-pMMA) (P1):** To a 20 mL scintillation vial was added MMA (0.5 g, 5.00 mmol, 9 eq.) and AnMA (0.15 g, 0.54 mmol, 1 eq.). In separate vials, CPADB (4.8 mg, 0.017 mmol, 0.03 eq.) and AIBN (0.96 mg, 0.006 mmol, 0.01 eq.) were dissolved in DMF. All three solutions were then transferred to a 25 mL Schlenk tube with a stir bar before more DMF was added to reach a total reaction volume of 5 mL. The solution was then degassed via three freeze-pump-thaw cycles before being placed in an oil bath at 70 °C and stirred for 16 hours. After 16 hours, the reaction was opened to air and quenched in liquid nitrogen to stop the polymerization reaction. The mixture was diluted with DCM and precipitated three times in methanol, and dried overnight in a vacuum oven to yield a pale pink powder as the product. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.51-7.51 (aromatic peaks from MMA and CPADB), 6.07 (O-CH<sub>2</sub>-An), (3.59-3.51, CH<sub>3</sub>-O), (1.82-0.84, aliphatic protons from MMA and AnMA). SEC (THF, MALS): *M<sub>n</sub>* = 47.6 kDa, *Đ* (1.11).

**Synthesis of P2.** A similar procedure to the synthesis of P1 was followed, but MMA (0.44 g, 4.4 mmol, 8 eq.) and AnMA (0.3 g, 1.08 mmol, 2 eq.) were used in the process. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.48-7.47 (aromatic peaks from MMA and CPADB), 6.05 (O-CH<sub>2</sub>-An), (3.59-3.50, CH<sub>3</sub>-O), (1.79-0.78, aliphatic protons from MMA and AnMA). SEC (THF, MALS): *M<sub>n</sub>* = 51.0 kDa, *Đ* (1.15).

### Dimerization of anthracene via TTA-UC

A 10 mL solution of PtOEP (0.43 mg) and anthracene (10 mg) in acetonitrile was made in an amber 20 mL scintillation vial. The solution was transferred to a 25 mL Schlenk tube and degassed via three freeze-pump-thaw cycles and then filled with argon before 3 mL was transferred into an air-tight cuvette. The cuvette was then irradiated with 532 nm light, with UV-vis absorbance spectra taken at 15 minute intervals. After 24 hours, the solvent was removed under reduced pressure to yield a pink

powder. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ (ppm) = 6.9 (m, aromatic), 6.8 (m, aromatic) 4.52 (s, bridgehead methylene).

### Synthesis of SCNPs via UV radiation

The following procedure was used for each of the two polymers, P1 and P2. A 10 mL solution of the polymer (0.1 mg/mL) in THF was made in an amber 20 mL scintillation vial. The solution was transferred to a 25 mL Schlenk tube and degassed via three freeze-pump-thaw cycles. After degassing, the tube was filled with argon before the solution was transferred to an airtight 3 mL quartz cuvette. The cuvette was then irradiated with a UV lamp at 366 nm, with UV-vis absorbance spectra taken at one minute intervals for 15 minutes.

### Synthesis of SCNPs via TTA-UC

The following procedure was used for each of the two polymers, P1 and P2. A 10 mL solution of PtOEP (0.0125 mg/mL) and the polymer (0.1 mg/mL) in THF was made in an amber 20 mL scintillation vial. The solution was transferred to a 25 mL Schlenk tube and degassed via three freeze-pump-thaw cycles. After degassing, the tube was filled with argon before the solution was transferred to an airtight 3 mL quartz cuvette. The cuvette was then irradiated with a 532 nm light for 24 hours.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

1. Y. C. Simon and C. Weder, *J. Mater. Chem.*, 2012, **22**, 20817.
2. J. Zhao, S. Ji and H. Guo, *RSC Advances*, 2011, **1**, 937-950.
3. X. Jiang, X. Guo, J. Peng, D. Zhao and Y. Ma, *ACS Appl. Mater. Interfaces*, 2016, **8**, 11441-11449.
4. T. Ogawa, N. Yanai, A. Monguzzi and N. Kimizuka, *Sci. Rep.*, 2015, **5**, 10882.
5. T. Wu and N. R. Branda, *Chem. Commun.*, 2016, **52**, 8636-8644.
6. C. A. Parker and C. G. Hatchard, *Proc. Royal Soc. A*, 1962, **269**, 574-584.
7. X. Yu, X. Cao, X. Chen, N. Ayres and P. Zhang, *Chem. Commun.*, 2015, **51**, 588-591.

8. S. P. Hill, T. Dilbeck, E. Baduelli and K. Hanson, *ACS Energy Lett.*, 2016, **1**, 3-8.
9. Q. Liu, W. Feng, T. Yang, T. Yi and F. Li, *Nat. Protoc.*, 2013, **8**, 2033.
10. R. R. Islangulov and F. N. Castellano, *Angew. Chem. Int. Ed. Engl.*, 2006, **45**, 5957-5959.
11. J. L. Charlton, R. Dabestani and J. Saltiel, *J. Am. Chem. Soc.*, 1983, **105**, 3473-3476.
12. J. Willenbacher, O. Altintas, V. Trouillet, N. Knöfel, M. J. Monteiro, P. W. Roesky and C. Barner-Kowollik, *Polym. Chem.*, 2015, **6**, 4358-4365.
13. T. Akagi, P. Piyapakorn and M. Akashi, *Langmuir*, 2012, **28**, 5249-5256.
14. M. A. J. Gillissen, I. K. Voets, E. W. Meijer and A. R. A. Palmans, *Polym. Chem.*, 2012, **3**, 3166-3174.
15. C. K. Lyon, A. Prasher, A. M. Hanlon, B. T. Tuten, C. A. Tooley, P. G. Frank and E. B. Berda, *Polym. Chem.*, 2015, **6**, 181-197.
16. W. J. Wedemeyer, E. Welker, M. Narayan and H. A. Scheraga, *Biochemistry*, 2000, **39**, 4207-4216.
17. V. A. Davankov, M. M. Ilyin, M. P. Tsyurupa, G. I. Timofeeva and L. V. Dubrovina, *Macromolecules*, 1996, **29**, 8398-8403.
18. B. T. Tuten, D. Chao, C. K. Lyon and E. B. Berda, *Polym. Chem.*, 2012, **3**, 3068-3071.
19. A. Sanchez-Sanchez, I. Pérez-Baena and J. Pomposo, *Molecules*, 2013, **18**, 3339.
20. T. S. Fischer, D. Schulze-Sünninghausen, B. Luy, O. Altintas and C. Barner-Kowollik, *Angew. Chem. Int. Ed.*, 2016, **55**, 11276-11280.
21. E. Harth, B. V. Horn, V. Y. Lee, D. S. Germack, C. P. Gonzales, R. D. Miller and C. J. Hawker, *J. Am. Chem. Soc.*, 2002, **124**, 8653-8660.
22. N. Hosono, A. M. Kushner, J. Chung, A. R. A. Palmans, Z. Guan and E. W. Meijer, *J. Am. Chem. Soc.*, 2015, **137**, 6880-6888.
23. P. G. Frank, B. T. Tuten, A. Prasher, D. Chao and E. B. Berda, *Macromol. Rapid Commun.*, 2014, **35**, 249-253.
24. R. Vadrucci, A. Monguzzi, F. Saenz, B. D. Wilts, Y. C. Simon and C. Weder, *Adv. Mater.*, 2017, **29**, 1702992-n/a.
25. A. K. Bansal, W. Holzer, A. Penzkofer and T. Tsuboi, *Chem. Phys.*, 2006, **330**, 118-129.
26. G. W. Breton and X. Vang, *J. Chem. Educ.*, 1998, **75**, 81.
27. S. Shanmugam, J. Xu and C. Boyer, *J. Am. Chem. Soc.*, 2015, **137**, 9174-9185.
28. E. Blasco, B. T. Tuten, H. Frisch, A. Lederer and C. Barner-Kowollik, *Polym. Chem.*, 2017, **8**, 5845-5851.
29. M. Haring, R. Perez-Ruiz, A. Jacobi von Wangelin and D. D. Diaz, *Chem. Commun.*, 2015, **51**, 16848-16851.
30. C. Alvarez-Lorenzo, L. Bromberg and A. Concheiro, *Photochem. Photobiol.*, 2009, **85**, 848-860.
31. G. Huh, K.-O. Kwon, S.-H. Cha, S.-W. Yoon, M. Y. Lee and J.-C. Lee, *J. Appl. Polym. Sci.*, 2009, **114**, 2093-2100.