ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. Qian, F. Chen, Y. Chen, Y. Wang and W. Hu, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC07560J.

View Article Online
DOI: 10.1039/C7CC07560J

Journal Name

COMMUNICATION

Photolysis of Polymeric Self-Assembly Controlled by Donor-Acceptor Interaction

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

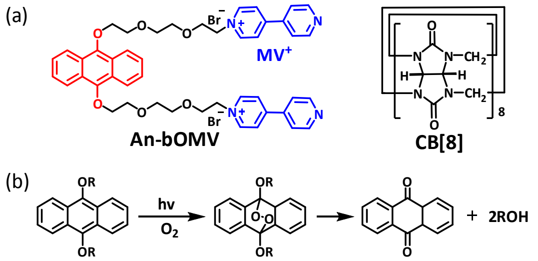
www.rsc.org/

Tingjuan Qian,[a] Feiyi Chen,[a] Yulan Chen,*[a] Yi-Xuan Wang*[a] and Wenping Hu[a]

A photodegradable supramolecular polymer was constructed with cucurbit[8]uril (CB[8]) and alkoxyanthracene guest. The monomeric unit was photostable because of the intramolecular donor-acceptor interaction. However, upon complexation with CB[8], photolysis of alkoxyanthracene was enhanced, which endowed the supramolecular polymer with great photoreactivity.

Photo-directed degradation of polymeric material is of great interest in both scientific research and practical applications for the development of optoelectronic devices, smart materials, targeted therapy and tissue engineering systems.[1] Numerous photoswitchable chromophores have been incorporated into polymeric scaffolds, such as azobenzene, spiropyran, and dithienylethene derivatives, yielding reversibly photoresponsive polymers.[2] Comparatively, photocleavable groups possess sufficient structural change upon light irradiation, making them as the most promising candidates for photodegradable materials.[3] A great deal of efforts has been made to enrich the photocleavable structure and to develop novel strategy for efficient photo-triggered depolymerization.[4]

Supramolecular polymerization has emerged as an alternative approach to the synthesis of smart polymers.[5] Since the monomeric units are connected by weak non-covalent interactions, most of supramolecular polymers exhibit remarkable responsiveness to external stimuli, which is obviously beneficial to the complete degradation. Among various noncovalent interactions, the host–guest chemistry based on cucurbit[8]uril (**CB[8]**) has played an important role in the development of exquisite polymeric materials.[6] It is not only because of the strong binding affinities of **CB[8]** as the macrocyclic host toward positively charged guests, but also ascribable to its unique tendency to include homogenous dimer of two conjugated molecules or heterogeneous charge transfer (CT) complex between electron acceptor and electron donor.[7] Additionally, donor-acceptor (D-A) interactions are also widely used to produce supramolecular architectures.[8] On the basis of these concepts, we propose a design strategy for the preparation of photodegradable polymer from photo-inert monomers, by **CB[8]**-mediated self-assembly. Anthracene attached with electron-donating groups at 9,10-positions shows efficient photodecomposition, owing to its high electron density.[9] Moreover, its photolysis was reported to be significantly enhanced within amphiphilic self-assembly, endowing alkoxyanthracene with promising application in photocleavable units.[10] Herein, the pro-photoactive polymeric monomers **An-bOMV** was synthesized, composed of 9,10-dialkoxyanthracenes as electron-rich cores and monocharged 4,4-bipyridiniums (**MV$^+$**) as electron-deficient terminals (Scheme 1). **MV$^+$** was proposed to enhance the photostability of guest molecules through reducing the electron density of aromatic cores by D-A interactions.[11] Oligoethylene glycol chains were used as linkers to bestow water-solubility and flexibility on the guest molecule. Furthermore, D-A interactions were expected to be diminished in the presence of **CB[8]**, leading to photoactive supramolecular assemblies. In general, **CB[8]** acts as the host to enhance the D-A interaction via simultaneous encapsulation of the heterogeneous CT complex. But in this work, we use it to weaken the D-A interaction by inclusion of homogenous dimer of two electron-



Scheme 1. (a) Chemical structures of photoactive guest and **CB[8]**. (b) Mechanism of photodecomposition of 9,10-dialkoxyanthracene.

---

[a] Tianjin Key Laboratory of Molecular Optoelectronic Science, Department of Chemistry, School of Science, Tianjin University, and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China
*E-mail: yulan.chen@tju.edu.cn; yx_wang@tju.edu.cn

Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7CC07560J

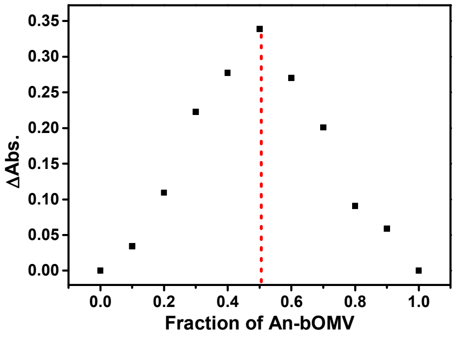


Figure 1. Job plot for **An-bOMV**−**CB[8]** system in water at 25 °C. [**An-bOMV**] + [**CB[8]**] = 0.03 mM.

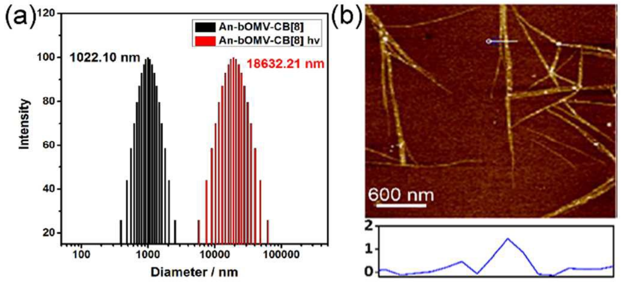


Figure 2. (a) DLS results of aqueous solutions of **An-bOMV**−**CB[8]** complexes before and after light irradiation for 2 h. [**An-bOMV**] = [**CB[8]**] = 0.5 mM. (b) AFM image of **An-bOMV**−**CB[8]** complexes.

deficient **MV**$^+$ through ion-dipole interactions,[12] since the 9,10-substituted anthracene goes against threading into the **CB[8]** cavity because of its bulk effect.[13] Contrary to the typical photoresponsive systems, polymeric monomers in this work are more stable to light than the polymeric species, which is quite beneficial to the practical production and application. In addition, this strategy offers a new thinking for the development of photoactive polymeric materials.

To investigate the host–guest complexation, the binding stoichiometry between **CB[8]** and anthracene guest was explored by UV−vis spectroscopic titration with a fixed guest concentration at 10.0 μM (Figure S1 in Supporting Information). Upon addition of **CB[8]**, an inflection point was observed at 1:1 (**CB[8]**:**An-bOMV**) molar ratio in the plot of the optical absorbance for **An-bOMV** (recorded at 260 nm), which indicated that **An-bOMV** bound to **CB[8]** in 1:1 (or *n*:*n*) ratio. Moreover, a peak in the Job plot at the molar fraction of 0.5 was found (Figure 1), again confirming the 1:1 (or *n*:*n*) binding stoichiometry. The binding of **MV**$^+$ moieties in **An-bOMV** with **CB[8]** was testified by cyclic voltammetry. In the presence of **CB[8]**, a moderate positive shift of the first reduction peak of **An-bOMV** was observed, accompanied with a great negative shift for the second peak (Figure S2 in Supporting Information), suggesting the encapsulation of a pair of the **MV**$^+$ moieties into the cavity of **CB[8]**.[14] Furthermore, NOE correlation was found between the protons H_1 and H_2 of **An-bOMV**−**CB[8]** complexes (Figure S3 in Supporting Information), indicating a head-to-tail stacking of the two included **MV**$^+$ units.[15] Because of such a unique binding mode of terminal **MV**$^+$ moieties for **CB[8]** in 2:1 molar ratio,[16] the binary complexes may spontaneously polymerize to form linear self-assemblies. ^{1}H NMR spectra were measured to study the process. As shown in Figure S4 (Supporting Information), the signals of protons of **An-bOMV** and **CB[8]** were both distinctly broadened after complexation in equimolar amounts (1.0 mM), suggesting supramolecular polymers may be generated.[17] It should be noted that a similar guest molecule with alkyl-chain-linked **MV**$^+$ units was reported to form the bi-molecular complex with **CB[8]**, in which **MV**$^+$ groups joined together in head to head fashion in the **CB[8]** cavity. The resulting molecular loop could be well-defined in ^{1}H NMR spectra because of its low-molecular-weight nature.[18] On the contrary, in our case, the steric effect of anthracene group and the electrostatic repulsion between **MV**$^+$ moieties may facilitate the stacking of **MV**$^+$ units in a head to tail fashion when included by **CB[8]**,[19] leading to the *n*:*n* polymeric assembly.

We further performed viscosity measurements to validate the formation of the supramolecular polymer in aqueous solution. As shown in Figure S5 in Supporting Information, the specific viscosity of the solution of **An-bOMV**−**CB[8]** complex varied exponentially with its concentration, which indicated the formation of interacting polymeric assemblies with increasing sizes.[20] In contrast, the solution of free **An-bOMV** showed a linear change in specific viscosity under the same conditions, implying that neither significant supramolecular polymerisation nor physical entanglements occurred.[20] Besides, according to the dynamic light scattering (DLS) measurement (Figure 2a), the hydrodynamic diameter distribution of the solution of **An-bOMV**−**CB[8]** complex was determined at about 1000 nm, also confirming the appearance of assembled species.[21] AFM was further used to explore the morphology of **An-bOMV**−**CB[8]** assemblies. As shown in Figure 2b, linear nano-structures with lengths in the micron range were observed, and the heights of assemblies were about 1.7 nm, which are in nice agreement with the size of outer diameter of **CB[8]**.[7a] Therefore, it can be concluded that **An-bOMV** guest bound with **CB[8]**, yielding supramolecular polymers.

UV−vis absorption measurements were performed to monitor the D-A interactions of guest in the absence and presence of **CB[8]**. As shown in Figure 3a, the DMSO solution of **An-bOMV** exhibited typical absorption bands of anthracene in the range of 340−430 nm. Comparatively, a broad band appeared above 430 nm for the aqueous solution of **An-bOMV**, which could probably be assigned to the absorption of charge transfer (CT) complex, driven by the D-A interaction between alkoxyanthracene and **MV**$^+$. This is because that the CT process is dramatically enhanced in the solvent with higher dielectric constant.[22] Such differences in modes of D-A complexation could also be supported by the ^{1}H NMR spectra of **An-bOMV** measured in D_2O and DMSO-d_6 (Figure S6 in Supporting Information). Compared with those observed in DMSO-d_6, the signals of **MV**$^+$ protons observed in D_2O exhibited remarkable upfield shifts, which was attributed to the ring current effect of the anthracene, indicative of a closer

View Article Online
DOI: 10.1039/C7CC07560J

correlation between **MV**$^+$ and anthracene in water. After addition of **CB[8]**, the CT absorption band clearly disappeared, illustrating that such D-A interaction in **An-bOMV** was destroyed, which resulted from the encapsulation of **MV**$^+$ moieties of **An-bOMV** by **CB[8]**. Fluorescence spectroscopy was also used to testify the evolution of D-A interactions (Figure 3b). The emission intensity of the **An-bOMV** was significantly increased after binding with **CB[8]**, ascribed to that the host–guest inclusion prevented the approximation of **MV**$^+$ to the fluorophore (anthracene) and thereby shut down the photoinduced electron transfer (PET) from anthracene to **MV**$^+$.[23] Concentration-dependent UV–vis absorption measurements were then executed and the results were shown in Figure S7 (Supporting Information). The CT absorptions of free **An-bOMV** in water showed appreciable linear changes as the concentration increased from 0.1 mM to 1.0 mM, which clearly excluded the possibility of intermolecular D-A interaction. Combined with the molecular structures, we inferred the modes for intramolecular D-A complexation in this work (Figure 3c). **An-bOMV**, with long and flexible linkers, can fold to bring the electron-acceptor (**MV**$^+$) into close association with the electron-donor (alkoxyanthracene). When encapsulated by **CB[8]**, **MV**$^+$ of **An-bOMV** was separated from alkoxyanthracene and the big spatial gap pronouncedly weakened the D-A interaction, accompanied by the recovery of the photoactivity of alkoxyanthracene (e.g., the fluorescent emission).

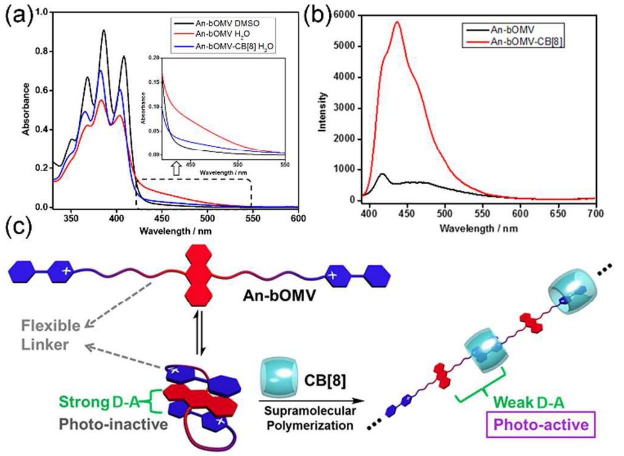


Figure 3. (a) UV–vis absorption spectra of **An-bOMV** in DMSO, and **An-bOMV** with and without **CB[8]** in water. (b) Fluorescence spectra of **An-bOMV** with and without **CB[8]** in water (λ_{ex} = 365 nm). [**An-bOMV**] = [**CB[8]**] = 0.1 mM. (c) Schematic illustrations of evolutions of D-A interactions and photoactivities induced by supramolecular polymerization.

9,10-dialkoxy-substituted anthracene was reported to trap singlet oxygen upon light irradiation, yielding endoperoxide followed by further decomposition.[24] Therefore, UV–vis absorption measurements were performed to monitor the photolysis of **An-bOMV** as free monomers and within polymeric assemblies. As shown in Figures 4 and S8 (Supporting Information), when free **An-bOMV** was irradiated for 60 min in water, the typical absorption peaks of anthracene group in 330–430 nm decreased by 35%. Comparatively, more than 70% of **An-bOMV** decomposed upon irradiation in the same condition but after self-assembly with **CB[8]**, which implied that the photoactivity of **An-bOMV** was significantly enhanced via host–guest chemistry. We further identified the photolytic products for **An-bOMV** and the polymeric assemblies by ^{1}H NMR, EI-MS and HR-ESI-MS measurements, and the generation of anthraquinone and relevant alkanols was confirmed for all the systems (Figures S9–S12 in Supporting Information). These results suggested that **An-bOMV** underwent the same phototransformation as reported before and excluded the possibility that the changes in photoactivity were derived from different reaction routes. As the highly electron-rich 9,10-dialkoxyanthracene group enabled photolysis,[25] the D-A interaction between anthracene and electron-deficient **MV**$^+$ group should play essential roles in the mediation of photoactivity. The **MV**$^+$ group of free **An-bOMV** reduced the electron density of anthracene to a great extent through the strong intramolecular D-A interaction, making **An-bOMV** quite stable to light irradiation. When included by **CB[8]**, **MV**$^+$ group of **An-bOMV**–**CB[8]** assembly was efficiently separated from the electron-rich core, thus activating the photodecomposition. Therefore, we successfully controlled the photoreactivity of alkoxyanthracene by attaching electron-withdrawing groups with flexible oligoethylene glycol chains as linkers. The D-A interaction greatly affected the photodecomposition of anthracene which could be switched via host–guest chemistry. As a result, the supramolecular polymeric assembly of **An-bOMV** with **CB[8]** exhibited enhanced photoactivity than **An-bOMV** itself. In addition, viscosity measurements (Figure S5 in Supporting Information) show a linear relation between specific viscosity and substance concentration for the **An-bOMV**–**CB[8]** polymer after irradiation for 2 h, clearly proving the photo-induced depolymerisation. According to the DLS results (Figure 2a), the diameter distribution of the irradiated **An-bOMV**–**CB[8]** polymer was determined as ca. 18 μm, corresponding to the disappearance of supramolecular assembly and the yield of insoluble anthraquinone. Besides, linear structures could not

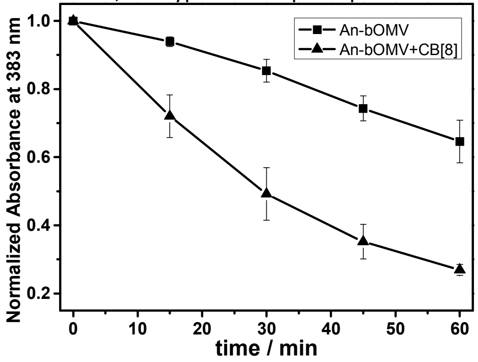


Figure 4. Normalized absorbance at 383 nm of free **An-bOMV** guest and **An-bOMV**–**CB[8]** assemblies upon light irradiation for different periods of time at pH 7. The trial was repeated by the same method for 3 times and concentrations of all the substances were kept at 0.1 mM.

View Article Online
DOI: 10.1039/C7CC07560J

be observed in the AFM image of irradiated polymer (Figure S13 in Supporting Information). Taken together, these results demonstrated that the **An-bOMV**–**CB[8]** polymer was fully decomposed.

In conclusion, we have successfully constructed supramolecular photodegradable assemblies based on the host–guest interactions between macrocyclic **CB[8]** and photo-decomposable guest (**An-bOMV**). Upon light irradiation, the 9,10-dialkoxyanthracene moiety of **An-bOMV** guest could slowly decompose into anthraquinone and alkanol. However, because of the reduction of D-A interactions, the photodecomposition was remarkably promoted after assembly with **CB[8]**, accompanied by the degradation of the linear supramolecular polymer. In other words, we developed a novel strategy, in which photodegradable polymer was built with light-inert monomers though self-assembly-mediated D-A interaction. This promising strategy can be used to construct various light-responsive polymeric materials, which have potential applications in the fields of photodynamic therapy and the photodegradation of pollutants.

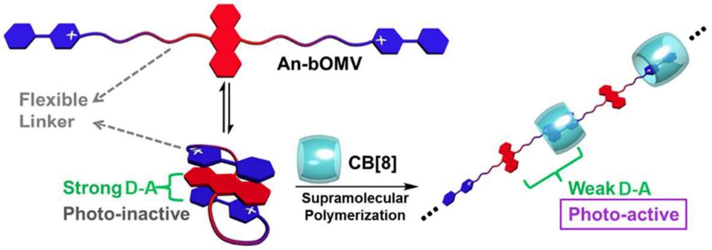
This work was supported by the National Key Research and Development Program of China (Grants 2016YFB0401100 and 2017YFA0204503) and National Natural Science Foundation of China (Grants 21604062 and 21522405). The authors are grateful to Prof. Long Chen (Tianjin University) for his help with photolysis measurement.

Notes and references

1. (a) J.-A. Lv, Y. Y. Liu, J. Wei, E. Q. Chen, L. Qin and Y. l. Yu, *Nature*, 2016, **537**, 179–184; (b) A. M. Kloxin, A. M. Kasko, C. N. Salinas and K. S. Anseth, *Science*, 2009, **324**, 59–63; (c) Q. Zhang, D.-H. Qu, X. Ma and H. Tian, *Chem. Commun.*, 2013, **49**, 9800–9802.
2. (a) J. del Barrio, S. T. J. Ryan, P. G. Jambrina, E. Rosta and O. A. Scherman, *J. Am. Chem. Soc.*, 2016, **138**, 5745–5748; (b) J. F. Gohy and Y. Zhao, *Chem. Soc. Rev.*, 2013, **42**, 7117–7129.
3. (a) P. Klan, T. Šolomek, C. G. Bochet, A. Blanc, R. Givens, M. Rubina, V. Popik, A. Kostikov and J. Wirz, *Chem. Rev.*, 2013, **113**, 119–191; (b) J. S. Katz, S. Zhong, B. G. Ricart, D. J. Pochan, D. A. Hammer and J. A. Burdick, *J. Am. Chem. Soc.*, 2010, **132**, 3654–3655.
4. (a) G. H. Liu, X. R. Wang, J. M. Hu, G. Y. Zhang and S. Y. Liu, *J. Am. Chem. Soc.*, 2014, **136**, 7492–7497; (b) S. B. Ji, W. Cao, Y. Yu and H. P. Xu, *Angew. Chem., Int. Ed.*, 2014, **53**, 6781–6785; (c) J. Araki, Y. Honda and Y. Kohsaka, *Polymer*, 2017, **125**, 134–137; (d) S. W. Guo, X. Liu, C. H. Yao, C. X. Lu, Q. X. Chen, X.-Y. Hu and L. Y. Wang, *Chem. Commun.,* 2016, **52**, 10751–10754; (e) X. Zhang, Y. P. Wang, G. Li, Z. T. Liu, Z. W. Liu and J. Q. Jiang, *Macromol. Rapid Commun.*, 2017, **38**, 1600543; (f) S. Chatterjeea and S. Ramakrishnan, *Chem. Commun.*, 2013, **49**, 11041–11043.
5. (a) Y. T. Kang, X. Y. Tang, Z. G. Cai and X. Zhang, *Adv. Funct. Mater.*, 2016, **26**, 8920–8931; (b) X.-L. Ni, X. Xiao, H. Cong, L.-L. Liang, K. Cheng, X.-J. Cheng, N.-N. Ji, Q.-J. Zhu, S.-F. Xue and Z. Tao, *Chem. Soc. Rev.*, 2013, **42**, 9480–9508; (c) Z. Q. Yan, Q. H. Huang, W. T. Liang, X. K. Yu, D. Y. Zhou, W. H. Wu, J. J. Chruma and C. Yang, *Org. Lett.*, 2017, **19**, 898–901; (d) W. Tian, X. X. Li and J. X. Wang, *Chem. Commun.*, 2017, **53**, 2531–2542; (e) C. Li, M. J. Rowland, Y. Shao, T. Y. Cao, C. Chen, H. Y. Jia, X. Zhou, Z. Q. Yang, O. A. Scherman and D. S. Liu, *Adv. Mater.*, 2015, **27**, 3298–3304; (f) B. V. K. J. Schmidt and C. Barner-Kowollik, *Angew. Chem., Int. Ed.*, 2017, **56**, 8350–8369.
6. (a) A. I. Day, A. P. Arnold, J. B. Rodneya and S. Barry, *J. Org. Chem.*, 2001, **66**, 8094–8100; (b) J. Heo, S. Y. Kim, D. Whang and K. Kim, *Angew. Chem., Int. Ed.*, 1999, **38**, 641–643; (c) L. L. Zhu, M. J. Zhu and Y. L. Zhao, *Chem. Plus. Chem.*, 2017, **82**, 30–41.
7. (a) S. J. Barrow, S. Kasera, M. J. Rowland, J. del Barrio and O. A. Scherman, *Chem. Rev.*, 2015, **115**, 12320–12406; (b) M. Kumar and S. J. George, *Chem. Asian J.*, 2014, **9**, 2427–2431.
8. (a) Y.-K. Tian, Y.-F. Han, Z.-S. Yang and F. Wang, *Macromolecules*, 2016, **49**, 6455–6461; (b) A. Das and S. Ghosh, *Angew. Chem., Int. Ed.*, 2014, **53**, 2038–2054; (c) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev*., 2005, **105**, 1491–1546; (d) J. Hu, P. Y. Wang, Y. Lin, S. Yang, B. Song and Q. Wang, *Org. Biomol. Chem.*, 2014, **12**, 4820–4823; (e) S. De and S. Ramakrishnan, *Angew. Chem., Int. Ed.*, 2004, **43**, 3264–3268.
9. T. Yamamoto, S. Yagyu and Y. Tezuka, *J. Am. Chem. Soc.*, 2016, **138**, 3904–3911.
10. Y.-X. Wang, Y.-M. Zhang and Y. Liu, *J. Am. Chem. Soc.*, 2015, **137**, 4543–4549.
11. W. G. Santos, D. S. Budkina, V. M. Deflon, A. N. Tarnovsky, D. R. Cardoso and M. D. E. Forbes, *J. Am. Chem. Soc.*, 2017, **139**, 7681–7684.
12. (a) F. Lin, T.-G. Zhan, T.-Y. Zhou, K.-D. Zhang, G.-Y. Li, J. Wu and X. Zhao, *Chem. Commun.*, 2014, **50**, 7982–7985; (b) K.-D. Zhang, J. Tian, D. Hanifi, Y. B. Zhang, A. C.-H. Sue, T.-Y. Zhou, L. Zhang, X. Zhao, Y. Liu and Z.-T. Li, *J. Am. Chem. Soc.*, 2013, **135**, 17913–17918.
13. F. Biedermann, I. Ross and O. A. Scherman, *Polym. Chem.*, 2014, **5**, 5375–5382.
14. W. S. Jeon, A. Y. Ziganshina, J. W. Lee, Y. H. Ko, J.-K. Kang, C. Lee and K. Kim, *Angew. Chem., Int. Ed.*, 2003, **42**, 4097–4100.
15. Z.-J. Zhang, H.-Y. Zhang, L. Chen and Y. Liu, *J. Org. Chem.*, 2011, **76**, 8270–8276.
16. J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim and K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621–630.
17. Y. L. Liu, Y. Yu, J. Gao, Z. Q. Wang and X. Zhang, *Angew. Chem., Int. Ed.*, 2010, **49**, 6576–6579.
18. Z.-J. Zhang, Y.-M. Zhang and Y. Liu, *J. Org. Chem.*, 2011, **76**, 4682–4685.
19. S. Schoder and C. A. Schalley, *Chem. Commun.*, 2017, **53**, 9546–9549.
20. H. Qian, D.-S. Guo and Yu Liu, *Asian J. Org. Chem*., 2012, **1**, 155–159.
21. Y. Lan, Y. C. Wu, A. Karas and O. A. Scherman, *Angew. Chem., Int. Ed.*, 2014, **53**, 2166–2169.
22. B.-R. Hyun, A. C. Bartnik, J.-K. Lee, H. I. L. F. Sun, J. J. Choi, Y Chujo, T. Hanrath, C. K. Ober and F. W. Wise, *Nano Lett.*, 2010, **10**, 318–323.
23. G. A. Davis, *J. Chem. Soc. Chem. Commun.*, 1973, 728–729. Y. Jiao, J.-F. Xu, Z. Q. Wang and X. Zhang, *ACS Appl. Mater. Interfaces,* 2017, **9**, 22635–22640.
24. D. Arian, L. Kovbasyuk and A. Mokhir, *J. Am. Chem. Soc.*, 2011, **133**, 3972–3980.
25. M. F. Powell, *J. Org. Chem.*, 1987, **52**, 56–61.

View Article Online
DOI: 10.1039/C7CC07560J

Table of Contents Entry



Photodegradable polymer was built with light-inert monomer though self-assembly-mediated donor-acceptor interaction.