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Multi-charged macrocycles as a platform for rapid and broad spectral photodecomposition of aromatic dyes[†]

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Four water-soluble macrocycles were chosen to explore the photodecomposition behaviours of quaternized 9-alkoxy-substituted anthracene (AnQA). Significantly, a highly charged macrocyclic skeleton leads to extremely close packing among the anthryl rings, providing a favourable hydrophobic environment for singlet oxygen, leading to rapid oxidation to produce the photoproducts under sunlight irradiation.

With the rapid spread of industrialization, environmental stains, especially the emerging organic contaminants (EOCs), have been seriously threatening human health and life.¹ Notably, industrial wastewater, which often contains various organic dyes, is one of the most serious contamination sources at the moment.² Currently, people are energetically looking for efficient means of pollutant management,³ most of which are in the form of pollutant separations, such as membrane separation,⁴ activated carbon adsorption,⁵ ion exchange on synthetic adsorbent resins⁶ and coagulation by chemical agents.7 Unfortunately, these traditional methods can only separate and enrich contaminants directly from wastewater, and cannot degrade pollutants at once because they just simply transfer organic dyes from water to another phase, thus causing secondary pollution.8 Consequently, the effective degradation of pollutants is an important goal at present. Photodegradation represents one of the increasingly vital topics in environmental improvement research, since it is capable of degrading organic contaminants irreversibly by using sunlight as the photolysis energy and the oxygen in the air as an oxidant under ambient conditions. Recently, some photodegradation processes based on supramolecular assembly via noncovalent interactions have been reported, which have provided insights into the supramolecular photochemistry field. For

example, Cao *et al.* reported a visible light activated photocatalyst assembled from α -Keggin type polysilicontungstate anions and cucurbit[6]uril *via* hydrogen bonding. This photocatalyst shows a good photocatalytic activity towards the degradation of methyl orange under visible light irradiation.⁹ Fan and coworkers used an optically active Sn(v) *meso*-tetraphenylporphine dichloride to initiate non-covalent self-assembly into hierarchical structured nanocrystals. The nanocrystals exhibited photocatalytic activities in the photodegradation of methyl orange pollutants.¹⁰ We also constructed an amphiphilic assembly based on the aggregation induced by *p*-sulfonatocalix[4]arene, which exhibited efficient photolysis under visible light in the presence of exogenous photosensitizers.¹¹ However, it is still a challenge to achieve rapid and broad spectral photodecomposition without adding exogenous photosensitizers at present.

It is well known that cyclodextrins, calixarenes, crown ethers and cucurbiturils have been widely employed in the fabrication of multi-responsive supramolecular assemblies via van der Waals, hydrogen bond, hydrophobic and electrostatic interactions, etc.¹² By modifying the macrocyclic skeleton with negative charges and introducing electrostatic interactions, the critical aggregation concentration of guest molecules can be reduced, and the overall compactness can be promoted.¹³ Following this idea, three multi-charged anionic macrocycles, namely sulfato-β-cyclodextrin (SCD), p-sulfonatocalix[6]arene (SC6A) and bis(4,8-disulfonato-1,5-naphtho)-32-crown-8 (DNC), were used to induce the amphiphilic assembly of a quaternary ammonium salt modified guest molecule AnQA so as to explore the most efficient effect of photodecomposition in the absence of exogenous photosensitizers (Scheme 1). On the other hand, cucurbituril was also tested owing to its high binding ability towards positively charged guest molecules. Although the cavity size of β-CD is similar to that of cucurbit[7]uril, cucurbit[8]uril (CB[8]) was selected herein owing to its stronger binding affinities towards the quaternary ammonium group of AnQA.²⁰

Since the AnQA molecule contains a hydrophilic cationic quaternary ammonium tail and a hydrophobic anthracene head, it can form an induced aggregate with multi-charged



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 $\label{eq:Scheme 1} \begin{array}{l} \mbox{Construction of the rapid and broad spectral photodecomposition system (for a table of all host molecules with their size see Table S1, ESI†). \end{array}$

macrocycles via electrostatic interactions. Firstly, the critical aggregation concentrations (CAC) of AnQA in the presence of different macrocycles were determined by monitoring the dependence of the optical transmittance at 460 nm on the concentration of AnQA. The optical transmittance of free AnQA at 460 nm showed no conspicuous change as the concentration increased from 0.01 to 0.10 mM (Fig. S4, ESI†), suggesting that the free AnQA cannot self-aggregate in this concentration range. Upon adding SCD or SC6A, the optical transmittance at 460 nm declined gradually with increasing concentration of AnQA due to the formation of large aggregates (Fig. 1a and c). According to the plot of optical transmittance at 460 nm versus the concentration of AnQA, there is an inflection point at 0.016 mM or 0.10 mM, corresponding to a complexation-induced CAC value of AnQA in the presence of SCD or SC6A, respectively (Fig. 1b and d). In contrast, the optical transmittance of AnQA at 460 nm showed no obvious change as the concentration increased upon the addition of DNC or CB[8] (Fig. S4, ESI⁺), probably because DNC

and CB[8] tend to form inclusion complexes, rather than induced aggregates with AnQA.

To determine the best molar ratio of SCD/AnQA or SC6A/AnQA intermolecular aggregates, the optical transmittance of AnQA at a fixed concentration (0.10 mM) was monitored while increasing the concentration of SCD or SC6A. In Fig. 2, at a fixed concentration of AnQA (0.10 mM), the transmittance at 460 nm first gradually decreased until reaching a minimum at a SCD concentration of 0.01 mM (Fig. 2a) or a SC6A concentration of 0.02 mM (Fig. 2c), and then increased upon further addition of SCD or SC6A. The decrease of the optical transmittance revealed that a large aggregate was formed. Then, the addition of an excessive amount of SCD or SC6A led to the formation of a simple inclusion complex accompanied by the disassembly of the aggregate, resulting in an increase in the optical transmittance. Accordingly, the optimum mixing ratio of the supramolecular aggregate was calculated as SCD: AnQA = 1:10 or SC6A: AnQA = 1:5 respectively (Fig. 2b and d). Additionally, a simple mixture of SCD with AnQA at the optimum molar ratio exhibited a clear Tyndall effect (Fig. S5, ESI[†]), indicating the existence of many aggregates. A control experiment showed that neither SCD nor AnQA exhibited a Tyndall effect, revealing that both SCD and AnQA did not form large self-aggregates under the same conditions.

Moreover, the SCD/AnQA aggregates exhibited a narrow size distribution with an average hydrodynamic diameter of 87.50 nm (Fig. S6, ESI†). TEM images showed a number of spherical nanostructures with diameters ranging from 20 to 200 nm, indicating the formation of supramolecular aggregates in the SCD/AnQA system. Meanwhile, zeta potential measurements gave an average zeta potential of -60.77 mV, indicating that the surface of the SCD/AnQA aggregate was mainly covered by SCD. Combining all the aforementioned results, we deduced a possible aggregation mechanism. The inherent electrostatic repulsion among the



Fig. 1 Optical transmittance of AnQA at different concentrations in the presence of 0.05 mM SCD (a), or SC6A (c). Dependence of the optical transmittance at 460 nm on AnQA concentration in the presence of 0.05 mM SCD (b), or SC6A (d).



Fig. 2 Optical transmittance of AnQA (0.10 mM) upon increasing the concentration of (a) SCD (0–0.08 mM), and (c) SC6A (0–0.08 mM) at 25 °C. Dependence of the optical transmittance at 460 nm on the SCD (b), and SC6A (d) concentration (0–0.08 mM) with a fixed AnQA concentration (0.10 mM) at 25 °C.

cationic quaternary ammonium tails on the free AnQA is unfavorable for the π - π stacking of the anthracene heads. However, the anthracene heads can stack with each other closely once the cationic tails are surrounded by the negatively charged SCD *via* electrostatic attractions. Since SCD exists as a mixture of CDs randomly substituted by sulfonated groups with an average substitution degree of 13, the resultant SCD/AnQA nanoparticles were inhomogeneous to some extent. In addition, we classified the spheres as a type of nanoparticle, since there was no definite evidence to prove whether they were hollow or solid.

Anthracene is known to be directly excited by ultraviolet radiation and is prone to react with singlet oxygen to form stable cyclic endoperoxides,14 whereas endoperoxides formed by 9-alkoxy-substituted anthracene derivatives undergo rearrangement and oxidation subsequently, resulting in the formation of anthraquinones and related alkanols (Scheme S2, ESI[†]).¹⁵ Accordingly, UV-Vis measurements were performed to monitor the photodecomposition of AnQA. In Fig. 3a, the absorption band (300-400 nm) corresponding to the anthracene moiety marginally decreased after the UV light irradiation at 365 nm, indicating that only a small amount of AnQA was decomposed in the presence of DNC or CB[8], which is similar to the case of free AnQA after 20 minutes of UV light irradiation at 365 nm (Fig. S7, ESI[†]). In contrast, when the macrocycle/AnQA system was irradiated, AnQA could be photodecomposed rapidly. Significantly, the photodegradation rate constants of AnQA in the presence of SCD, SC6A, DNC or CB[8] (0.01 mM for each) were calculated to be 0.5567 M⁻¹, 0.236 M⁻¹, 0.0103 M⁻¹ and 0.0011 M^{-1} (Fig. 3a). That is, the order of the photodegradation rate constant (K_d) of the macrocycle/AnQA system was SCD/ AnQA > SC6A/AnQA \gg DNC/AnQA > CB[8]/AnQA, and the K_d values of macrocycle-induced aggregates (SCD/AnQA and SC6A/ AnQA) were 23-506 times higher than the corresponding values of the macrocycle-based inclusion complexes (DNC/AnQA and CB[8]/AnQA). These results strongly prove that the macrocycleinduced aggregation plays an important role in promoting the photodecomposition. Moreover, the stability and reusability of the host multi-charged macrocyclic compounds during the photodecomposition were also investigated, demonstrating that all the hosts were in good shape and reusable during the



Fig. 3 (a) UV/Vis absorption spectra of 0.10 mM AnQA with 0.01 mM SCD, 0.02 mM SC6A, 0.01 mM SC6A, 0.01 mM DNC, and 0.01 mM CB[8] after UV irradiation at 365 nm for 5 min. Note that: before UV/Vis absorption tests were performed, an equal volume of ethanol solution was added to the sample solution to eliminate the scattering error from the assemblies and facilitate quantitative analysis. (b) TEM image of the SCD/AnQA assembly upon UV irradiation at 365 nm for 20 min (scale bar = 200 nm).

photodecomposition of the guest molecules. In addition, we also compare the photodegradation rate of SCD/AnQA (or SC6A/AnQA) aggregates at different macrocycle:AnQA molar ratios, and the results showed that the SCD/AnQA (or SC6A/AnQA) aggregate at the best molar ratio gave the highest photodegradation rate constant. Based on the above experiments, SCD is found to be the best multi-charged macrocycle for inducing aggregation and promoting photodecomposition. Therefore, SCD was selected as the macrocyclic model for subsequent experiments.

Compared with that of the free AnQA, the absorption band of the SCD/AnQA aggregates showed a redshift of about 10 nm, assigned to the π - π stacking and charge-transfer (CT) interactions.¹⁶ However, this absorption band decreased drastically upon UV irradiation for 20 minutes, accompanied by the formation of precipitates, which clearly indicated that the photodecomposition ability of AnQA was enhanced significantly after the SCD-induced aggregation. ¹H NMR and mass spectrometry (MALDI-TOFMS) were further employed to identify the photolysates of AnQA. After the UV irradiation at 365 nm for 10 minutes, the solution of the SCD/AnQA aggregate was lyophilized and then redissolved in DMSO-d₆ for ¹H NMR measurements. The ¹H NMR spectrum showed two new peaks at 8.22 and 7.94 ppm assigned to anthraquinones produced by the photochemical reaction (Fig. S8, ESI⁺). In addition, the m/z peak of trimethylamino-1-butanol at 132.14, assigned to the product of AnQA after the UV irradiation, was also observed in the MS spectrum (Fig. S9, ESI⁺). Since AnQA decomposes into insoluble anthraquinone and hydrophilic alkanol, the SCD/AnQA aggregate is expected to dissipate after the UV irradiation. As can be seen from the DLS measurement result, there is a wide size distribution with a large hydrodynamic diameter (up to 1 µm) after UV irradiation for 20 minutes (Fig. S10, ESI⁺). Besides, no spherical morphologies can be observed in the TEM image after the irradiation (Fig. 3b).

The photodecomposition of the SCD/AnQA aggregates at various irradiation wavelengths (500 nm, 600 nm, 670 nm and 700 nm) was also monitored by UV-Vis measurements. In Fig. S11-S14 (ESI⁺), only a small amount of free AnQA was decomposed after 40 minutes of light irradiation at different wavelengths. However, the absorption peaks of the anthracene moiety (340-400 nm) in the SCD/AnQA aggregate all decreased obviously after irradiation for 40 minutes at these wavelengths, which indicated that the SCD-induced aggregation can effectively accelerate the photodegradation process of AnQA at these wavelengths. For either the free AnQA or the SCD/AnQA aggregates, the photodecomposition rate under UV irradiation at 365 nm is the fastest (Fig. S15, ESI†). The results of mass spectrometry show that there are m/z peaks at 132.14 corresponding to trimethylamino-1butanol in the photolysates (Fig. S16, ESI[†]), which strongly proves that the photodecomposition occurs after irradiation with UV, visible and near-infrared lights.

Finally, we tested whether the SCD/AnQA aggregates could be photodecomposed under sunlight. After the samples were exposed to sunlight, UV light at 365 nm and darkness respectively for 20 minutes, the photodecomposition of the SCD/ AnQA aggregates was measured by high performance liquid

chromatography (HPLC). As shown in Fig. S17 (ESI⁺), AnQA (the peak at retention time = 4.0 min) can be fully photodecomposed in the presence of SCD under UV light irradiation at 365 nm or sunlight within 20 minutes, while the photodecomposition rate of AnQA is extremely slow in the absence of SCD. As expected, both the free AnQA and the SCD/AnQA aggregates were stable in darkness, showing no degradation. It is worth noting that the peak at retention time = 5.30 min in the HPLC chromatogram after the irradiation for 20 minutes was speculated to denote the photolysates of AnQA, i.e. anthraquinone. To prove this conjecture, we prepared a solution of anthraquinone for HPLC and mass spectrometric analysis. Fig. S17 (ESI[†]) shows that there is also a peak at retention time = 5.30 min in the HPLC chromatogram, which evidently confirms the peak assigned to the photolysates of AnOA, *i.e.* anthraquinone. Besides, the m/z peaks at 415.60 and 437.40 in the mass spectrum were assigned to the anthraquinone dimer and the adduct ion peak of the anthraquinone dimer respectively (Fig. S18, ESI⁺), which strongly proved that AnQA can be fully photodecomposed into anthraquinone under irradiation with sunlight for 20 minutes.

The photophysical properties of the SCD/AnQA aggregates were studied by fluorescence spectroscopy. Compared with the free AnQA, the emission intensity of the SCD/AnQA aggregates decreased significantly (Fig. S19, ESI[†]), which was mainly due to the π - π stacking and the aggregation quenching caused by intermolecular interactions. Although the fluorescence of the SCD/AnQA assembly is weaker than that of the free AnQA, the photodecomposition rate of AnOA is accelerated. It is worth noting that two kinds of agglomeration-promoting photolysis systems have been reported before. One is a photolysis system with retained photosensitivity;¹¹ the other is a photolysis system with reduced photosensitivity but that still promotes photodegradation, like the report by Wang et al.¹⁷ The present situation herein is similar to that of Wang. Therefore, we speculate that the mechanisms of this promoted photodecomposition system are mainly due to two aspects: (1) the aggregate provides a good hydrophobic environment, leading to the elongated lifetime of the singlet $oxygen;^{18}$ (2) the highly charged macrocyclic skeleton leads to extremely close packing among the anthracene rings, allowing the singlet oxygen to rapidly undergo the subsequent oxidation reactions with the nearby anthracene ring and ultimately leads to an increase in the photodegradation efficiency.¹⁹

In conclusion, we utilized some multi-charged macrocycles as platforms for the rapid and broad spectral photodecomposition of an aromatic dye (AnQA) in water. The inherent advantages of this system are: (1) the negative charges on the upper and/or lower edges of the macrocyclic cavity can greatly enhance the compact packing efficiency among anthracenes; (2) the supramolecular assembly exhibited excellent photodegradation ability upon wide spectral irradiation, including ultraviolet, visible and near infrared light irradiations, which may help potential influences in environmental applications; (3) AnQA can be fully photodegraded under sunlight without adding exogenous photosensitizers, which will not cause secondary environmental pollution.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 (a) D. J. Lapworth, N. Baran, M. E. Stuart and R. S. Ward, *Environ. Pollut.*, 2012, 163, 287; (b) Z. Aksu, *Process Biochem.*, 2005, 40, 997.
- 2 C. A. Martínez-Huitle and E. Brillas, Appl. Catal., B, 2009, 87, 105.
- 3 (a) F. Han, V. S. R. Kambala, M. Srinivasan, D. Rajarathnam and R. Naidu, *Appl. Catal.*, A, 2009, **359**, 25; (b) G. Crini, *Prog. Polym. Sci.*, 2005, **30**, 38.
- 4 (a) S. P. Dharupaneedi, S. K. Nataraj, M. Nadagouda, K. R. Reddy, S. S. Shukla and T. M. Aminabhavi, *Sep. Purif. Technol.*, 2019, 210, 850; (b) P. S. Goh and A. F. Ismail, *Desalination*, 2018, 434, 60.
- 5 (a) N. Kannan and M. M. Sundaram, *Dyes Pigm.*, 2001, **51**, 25; (b) P. K. Malik, *J. Hazard. Mater.*, 2004, **113**, 81.
- 6 (a) S. Akazdam, M. Chafi, W. Yassine, B. Gourich and N. Barka, J. Mater. Environ. Sci., 2017, 8, 784; (b) S. S. Beheraa, S. Dasb, P. K. Parhia, S. K. Tripathyb, R. K. Mohapatrac and M. Debatac, Desalin. Water Treat., 2017, 60, 249.
- 7 (a) G. Crini, *Bioresour. Technol.*, 2006, **97**, 1061; (b) V. K. Gupta and Suhas, *J. Environ. Manage.*, 2009, **90**, 2313.
- 8 I. K. Konstantinou and T. A. Albanis, Appl. Catal., B, 2004, 49, 1.
- 9 M. Cao, J. Lin, J. Lü, Y. You, T. Liu and R. Cao, J. Hazard. Mater., 2011, 186, 948.
- 10 Y. Zhong, Z. Wang, R. Zhang, F. Bai, H. Wu, R. Haddad and H. Fan, ACS Nano, 2014, 8, 827.
- 11 Y.-X. Wang, Y.-M. Zhang and Y. Liu, J. Am. Chem. Soc., 2015, 137, 4543.
- 12 (a) Y. Chen, F. Huang, Z.-T. Li and Y. Liu, Sci. China: Chem., 2018, 61, 979; (b) M. González-Béjar, P. Montes-Navajas, H. García and J. C. Scaiano, Langmuir, 2009, 25, 10490; (c) G. Chen and M. Jiang, Chem. Soc. Rev., 2011, 40, 2254–2266; (d) Y. Chen and Y. Liu, Chem. Soc. Rev., 2010, 39, 495; (e) F. Callari, S. Petralia and S. Sortino, Chem. Commun., 2006, 1009.
- (a) X. Han, Y. Chen, H.-L. Sun and Y. Liu, Asian J. Org. Chem., 2018, 7, 870; (b) X.-F. Hou, Y. Chen and Y. Liu, Soft Matter, 2015, 11, 2488; (c) X.-M. Chen, Y. Chen, X.-F. Hou, X. Wu, B.-H. Gu and Y. Liu, ACS Appl. Mater. Interfaces, 2018, 10, 24987; (d) J.-J. Li, Y. Chen, J. Yu, N. Cheng and Y. Liu, Adv. Mater., 2017, 29, 1701905.
- 14 (a) E. Bowen, *Discuss. Faraday Soc.*, 1953, 14, 143; (b) S. Kohtani,
 M. Tomohiro, K. Tokumura and R. Nakagaki, *Appl. Catal.*, B, 2005, 58, 265.
- (a) W. E. Barnett and L. L. Needham, J. Org. Chem., 1971, 36, 4134;
 (b) M. F. Powell, J. Org. Chem., 1987, 52, 56; (c) D. Arian, L. Kovbasyuk and A. Mokhir, J. Am. Chem. Soc., 2011, 133, 3972.
- 16 J. Hu, P. Wang, Y. Lin, J. Zhang, M. Smith, P. J. Pellechia, S. Yang, B. Song and Q. Wang, *Chem. – Eur. J.*, 2014, **20**, 7603.
- 17 S. Guo, X. Liu, C. Yao, C. Lu, Q. Chen, X.-Y. Hu and L. Wang, *Chem. Commun.*, 2016, 52, 10751.
- (a) P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, 1972, 94, 1029;
 (b) Y. Cheng, H. Cheng, C. Jiang, X. Qiu, K. Wang, W. Huan, A. Yuan, J. Wu and Y. Hu, *Nat. Commun.*, 2015, 6, 8785.
- 19 T. Tørring, S. Helmig, P. R. Ogilby and K. V. Gothelf, Acc. Chem. Res., 2014, 47, 1799.
- 20 (a) H. K. Young, K. Hyunuk, K. Youngkook and K. Kimoon, Angew. Chem., Int. Ed., 2008, 47, 4106; (b) K. I. Assaf, M. A. Alnajjar and W. M. Nau, Chem. Commun., 2018, 54, 1734.