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Hemicucurbit[6]uril-induced aerobic oxidation of heterocyclic compounds

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ABSTRACT

The aerobic oxidation of furan in aqueous solution in the presence of HemiQ[6] has been investigated, and the product furan-2,5-diol is stabilized by encapsulation of HemiQ[6], which could be transformed to the dione confirmation in acidic solution and escape from the macrocyclic compound. The ^{1}H NMR titration experiments of the host–guest interaction at different pH values suggest protonation should improve the encapsulation, and therefore an unique property that HemiQ[6] can be protonated has been revealed. The oxidizing kinetics suggests that the procedure is a consecutive reaction with a series of constants $k_1 = 2.9 \times 10^{-2}$ min^{-1}, $k_2 = 2.7 \times 10^{-2}$ min^{-1}, and $k_3 = 5.7 \times 10^{-3}$ min^{-1}, respectively. The kinetic investigation at pD = 2.0 indicates the HemiQ[6]-catalytic oxidation of furan could be accelerated by acidification. As a consequence, a plausible mechanism has been established on the above evidences. 2-Methylfuran is employed to give the product 2-methylfuran-5-ol exhibiting a satisfied activity in this aerobic oxidation with the supramolecular catalysis of HemiQ[6], but the oxidation of thiophene is very slow in either neutral or acidic condition.

1. Introduction

Cucurbit[*n*, *n* = 5–8, 10]urils (Q[*n*]s), are a family of artificial receptors in the shape of a pumpkin. They are made up of glycoluril units with methylene bridges [1–3]. In the pioneering work, the hydrophobic cavities were shown to provide an efficient nanospace for supramolecular catalysis. This portal effect, including hydrogen bonding, Van Der Waals, and ion–dipole interactions between the carbonyl portals of the host and the positive moiety on the guest, in many cases also produces prominent improvements in reactivity [4–6]. As a novel sort of supramolecular inhibitor, Qs have been employed to protect the active groups and decrease the toxicity of drugs [7–9]. The photochemical dimerizations of olefins, coumarins and cinnamic acids have been enhanced within Q [8], and the pre-orientation of substrates in the cavity induces an effective regio- and stereo-control [10–13]. The hydrolysis of benzoyl chlorides and oximes in the presence of Q[7] indicate that the supramolecular catalysis depends greatly on the substituent effect of the substrates, which influences the portal effect directly between the host–guest interactions [14,15]. In other cases of heterogeneous catalysis with Q[8], the substituent effect of the substrates also leads to the selective oxidation of alcohols [16,17].

Hemicucurbit[*n*, *n* = 6 or 12]urils (HemiQ[*n*], Scheme 1) are the new members in the cucurbituril family. They have more flexible structures, which, as a consequence, are more easily synthesized than the cucurbiturils, and their degree of oligomerization is controllable by varying the acidity [18]. Very recently, we successfully explored the HemiQ[6]-catalytic esterification reaction [19]. This has encouraged us to develop more novel supramolecular catalysis with these kinds of macrocyclic compounds. We report here the catalytic activities of HemiQ[6] for the aerobic oxidation of heterocyclic compounds, such as furans and thiophene.

Oxidation is a vital chemical process in organic synthesis. It produces oxygen-containing compounds such as alcohols, aldehydes, ketones, carboxylic acids and epoxides from hydrocarbons [20]. For user- and eco-friendly purposes, O_2 (or air) and H_2O_2 usually serve as the oxygen source. However, the direct application of O_2 can be hindered by a high energy barrier, due to the transition from the triplet state of the oxygen molecule to the singlet state [21]. To overcome this problem, lots of coordination compounds have been developed to capture and activate O_2. Cu^{2+}, Mn^{2+}, Pd^{2+} and Au^{+} are often used as the central metal cations in coordination compound catalysts [22–25]. This paper reports an alternative pathway, in which HemiQ[6] is used to allow the aerobic oxidation to be carried out under mild conditions via a supramolecular strategy (Scheme 1). The oxidation of furan usually cannot provide the hydroxyfuran product, which is an extremely unstable tautomers of the corresponding oxo derivative [26,27], the enol

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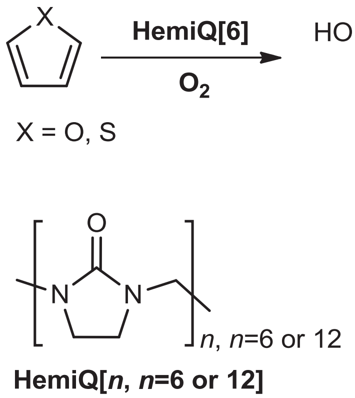


Scheme 1. Structures of the substrates and HemiQ[n, n = 6 or 12].

product, furan-2,5-diol, is able to be stabilized in the presence of HemiQ[6] hereinto.

2. Experimental

2.1. Materials and apparatus

HemiQ[n] (n = 6 or 12) samples were prepared and purified according to the method reported elsewhere [18] and were characterized by ^{1}H NMR, giving resonances for HemiQ[6] ($CDCl_3$, δ) at 3.40 ppm (s, 24H) and 4.67 ppm (s, 12H) and for HemiQ[12] ($CDCl_3$, δ) at 3.36 ppm (s, 24H) and 4.67 ppm (s, 12H). Q[n] was synthesized using methods developed in our laboratory [28]. Furan, 2-methylfuran and thiophene were obtained commercially (Tokyo Kasei Kogyo Co. Ltd.) and used without further purification.

^{1}H NMR spectra were recorded at 25 °C on a JEOL JNM-Al00 spectrometer (300 MHz) in D_2O, with TMS is used as an internal reference.

2.2. Catalytic oxidation experiments

The heterocyclic compounds (0.015 mmol) were added to 0.6 mL D_2O and then HemiQ[6] was added to the solution in a 1:1 ratio. The solution was heated to 65 °C and monitored by ^{1}H NMR over time. The reactant conversion was directly confirmed by ^{1}H NMR spectral data.

3. Results and discussion

The oxidation of furan in D_2O has been found to take place in the presence of HemiQ[6] from the ^{1}H NMR trace, while no reaction happens in the absence of the macrocyclic compound. As shown in Fig. 1, the two resonance signals from furan, at δ 6.5 and δ 7.6 ppm (Fig. 1a), become weaker as its deuterated aqueous solution is heated for 8 h, and a new singlet appears at δ 6.3 ppm (Fig. 1c). Comparing with Fig. 1b, the proton resonance of Hb on HemiQ[6] shows no shift, but the proton resonance of Ha becomes slightly split, which indicates the encapsulation of the product by the HemiQ[6]. The IR absorption of the hydroxyl group shows a slight blue shift, from 3436 to 3446 cm^{-1}, and the carbonyl groups on the binding HemiQ[6] show obvious differences in their IR absorption compared with the free host (Fig. S1, ESI). The proton resonance of —OH group appears at δ 1.07 ppm with the results of hydrogen–deuterium exchange action (Fig. S2, ESI). The above evidences show that furan is oxidized to furan-2,5-diol. The heated solution of furan and HemiQ[6] was acidified with DCl and neutralized with Na_2CO_3 followed by extraction with $CDCl_3$. This presence of the dione, dihydrofuran-2,5-dione (Fig. S3a, ESI) was confirmed, with the carbonyl group identified by IR by the absorption at 1683 cm^{-1} (Fig. S3b, ESI). On the other hand, that furan cannot be oxidized in deoxygenated aqueous solution (5% Na_2SO_3, and Ar atmosphere) in the presence or absence of HemiQ[6] suggests an aerobic process.

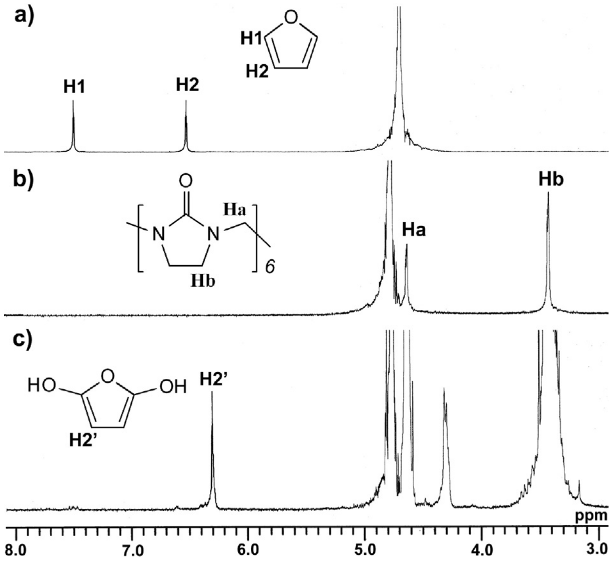


Fig. 1. ^{1}H NMR spectra of (a) furan; (b) HemiQ[6]; (c) a D_2O solution of furan after heating for 8 h in the presence of HemiQ[6].

In cucurbituril chemistry, the host–guest interactions are always characterized by changes of chemical shifts of the encapsulated guest in ^{1}H NMR. That is, the shielding effect leads to an upward shift of the resonance signals of guest when it is inserted into the core of the macrocyclic cavity. On the other hand, the deshielding effect from the carbonyl groups on the portals makes the ^{1}H NMR response of the guest remaining at the portal to shift down [3,9]. However, no chemical shift was observed for furan in the presence of HemiQ[6], as reported previously [19], simply broadening of the furan peaks and the appearance of a complicated resonance of HemiQ[6] (Fig. S4, ESI). Fortunately, the improvement of acidity allows the host–guest interaction model between furan and HemiQ[6] to be detected with ^{1}H NMR analysis (Fig. 2). In the presence of HemiQ[6] at pD 2.0, the resonance signals of all protons on the furan ring undergo a very slight downfield shift, which suggests that the guest remains in the deshielding area around the carbonyl groups on HemiQ[6] (Fig. 2a). The trace plots of these chemical shift changes from δ 6.28 to δ 6.35 ppm when the ratio of $C_{\mathrm{HemiQ[6]}}/C_{\mathrm{furan}}$ is up to 4.2:1 indicate a1:1 binding model with a weak association constant $K_a = (5.2 \pm 2.4) \times 10^{-2}$ L mol^{-1}. Accordingly, the host–guest interaction between furan and HemiQ[6] is likely to be improved by the participation of a proton.

The proposal in Miyahara's pioneering work [18], that HemiQ[6] binds to protons in the crystallographic structure, prompts us to investigate the protonation of this macrocyclic compound in solution. Comparing the ^{1}H NMR spectrum of HemiQ[6] in neutral and acidic D_2O (Fig. 3a), the proton resonance appears broadened in acidified solution (Fig. 3b). To provide clear evidence that a proton can be captured by this host, HemiQ[6] is dissolved in acidic aqueous solution (pH = 2.0) followed by extraction with $CDCl_3$. Subsequently, the spectrum of the organic layer shows the resonance signal of an active proton at δ 1.23 ppm (Fig. 3c). We propose that the presence of the proton, with its positive charge, decreases the repulsion between the electron-rich furan ring and the carbonyl groups on the HemiQ[6] and therefore stabilizes the host–guest interaction complex.

To understand the role of protons in this example of supramolecular catalysis, the kinetics of the aerobic oxidation with 1 equiv.

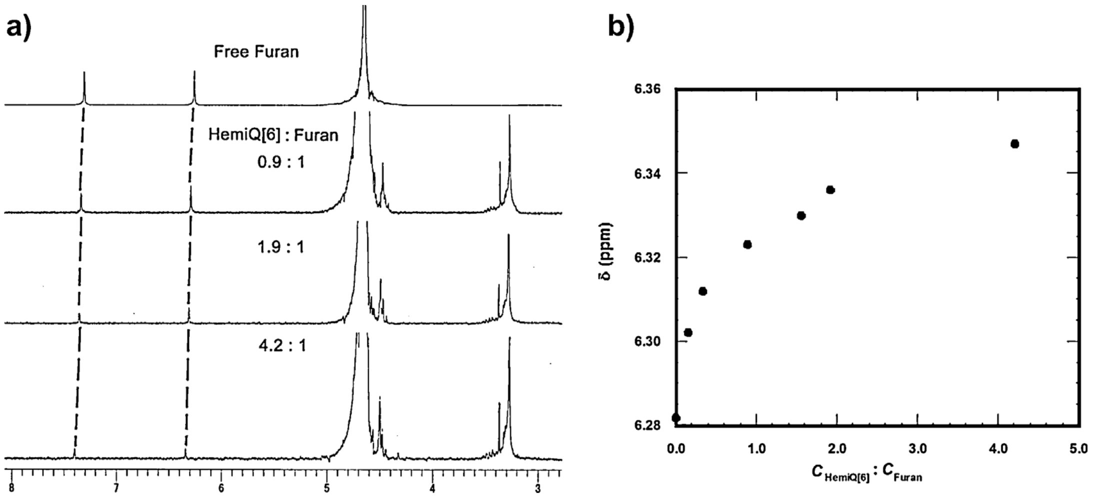
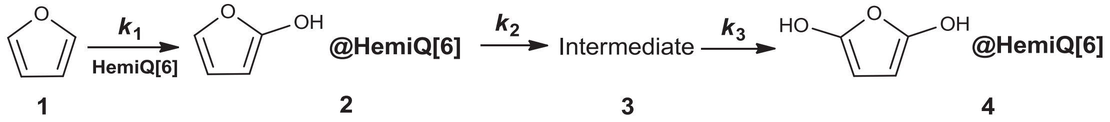


Fig. 2. (a) ^{1}H NMR titration of the host–guest interaction between furan and HemiQ[6] at pD = 2.0 (all attributions with reference to TMS); (b) changes of the chemical shift of proton H_2 on furan ring in the presence of different ratio of HemiQ[6].



Scheme 2. Oxidation of furan in the presence of HemiQ[6].

HemiQ[6] has been investigated at different pH values (Scheme 2). The ^{1}H NMR trace of the oxidation at pD = 6.3 shows that it is a typical consecutive reaction, with 3 steps (Fig. 4a). Firstly, furan is oxidized to furan-2-ol, which is the main product, accounting for more than 30% in this first stage. Subsequently, further oxidation weakens the proton resonance at δ 7.39 ppm and both resonance signals, at δ 6.32 and 6.25 ppm, show a positive shift. We conclude that there is an intermediate based on the furan-2-ol structure but without the β-H. However, the secondary hydroxyl is not yet fully bound. Finally, the oxidation produces a singlet at δ 6.20 ppm, which indicates that furan-2,5-diol is produced, with about 90% conversion.

The above reaction sequence can be described by the following kinetic formulas:

$$\frac{dC_{\text{furan}}}{dt} = -k_1 \cdot C_{\text{furan}} \tag{1}$$

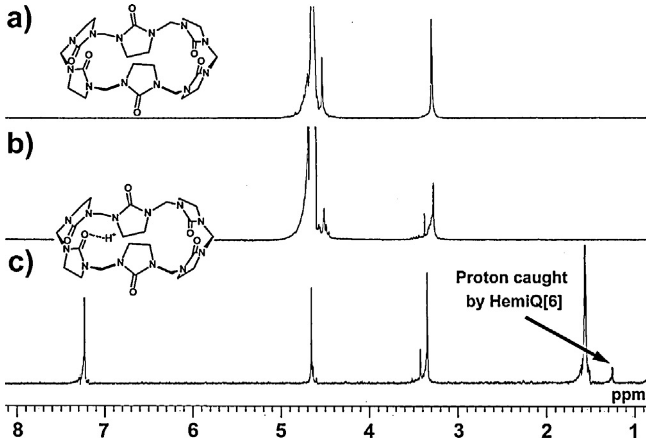


Fig. 3. ^{1}H NMR spectra of HemiQ[6] in (a) D_2O; (b) DCl/D_2O, pD = 2.0; (c) $CDCl_3$ extracted from DCl/D_2O at pH = 2.0.

$$\frac{dC_{\text{furan-2-ol}}}{dt} = k_1 \cdot C_{\text{furan}} - k_2 \cdot C_{\text{furan-2-ol}} \tag{2}$$

$$\frac{dC_{\text{furan-2,5-diol}}}{dt} = k_3 \cdot C_{\text{furan-2,5-diol}} \tag{3}$$

where k_1, k_2, and k_3 refer to the rate constants for the HemiQ[6]-induced aerobic oxidation reaction. These formulas can be integrated to give:

$$(C_{\text{furan}})_t = e^{-k_1 t} \tag{4}$$

$$(C_{\text{furan-2-ol}})_t = \frac{k_1}{k_2 - k_1} \cdot (e^{-k_1 t} - e^{-k_2 t}) \tag{5}$$

$$(C_{\text{furan-2,5-diol}})_t = 1 - e^{-k_3 t} \tag{6}$$

The distribution plots for furan, furan-2-ol and furan-2,5-diol at different times can be non-linearly fitted to formulas (4)–(6) (Fig. 4b–d) to give the corresponding kinetic constants $k_1 = 2.9 \times 10^{-2}\ \text{min}^{-1}$, $k_2 = 2.7 \times 10^{-2}\ \text{min}^{-1}$, and $k_3 = 5.7 \times 10^{-3}\ \text{min}^{-1}$. Clearly, the secondary oxidation is more difficult than the previous steps (k_3 is the smallest rate constant), so this should be the rate-determining step in the overall reaction. The oxidation of furan is slow down with the decreased amount of supramolecular catalyst, in the presence of 0.5 equiv. HemiQ[6], the rate constants are $k_1 = 5.5 \times 10^{-3}\ \text{min}^{-1}$, $k_2 = 5.1 \times 10^{-3}\ \text{min}^{-1}$, and $k_3 = 2.0 \times 10^{-3}\ \text{min}^{-1}$ (Fig. S5), while they are increased to $k_1 = 5.2 \times 10^{-2}\ \text{min}^{-1}$, $k_2 = 6.4 \times 10^{-2}\ \text{min}^{-1}$, and $k_3 = 1.3 \times 10^{-2}\ \text{min}^{-1}$ with 2.0 equiv. HemiQ[6] (Fig. S6).

The oxidation of furan in the presence of HemiQ[6] at pD = 2.0 has also been tracked using ^{1}H NMR spectra (Fig. 5a) and a similar process, involving three basic steps, has been found. However, the reaction rates for all stages are clearly faster than those in neutral conditions, as found from fitting the kinetic plots using formulas (4)–(6) (Fig. 5b–d). The improvement of the kinetic constants ($k_1 = 7.2 \times 10^{-2}\ \text{min}^{-1}$, $k_2 = 5.2 \times 10^{-2}\ \text{min}^{-1}$, and $k_3 = 1.4 \times 10^{-2}\ \text{min}^{-1}$) demonstrates that the oxidation can be accelerated in acid conditions, that is, the proton affects not only

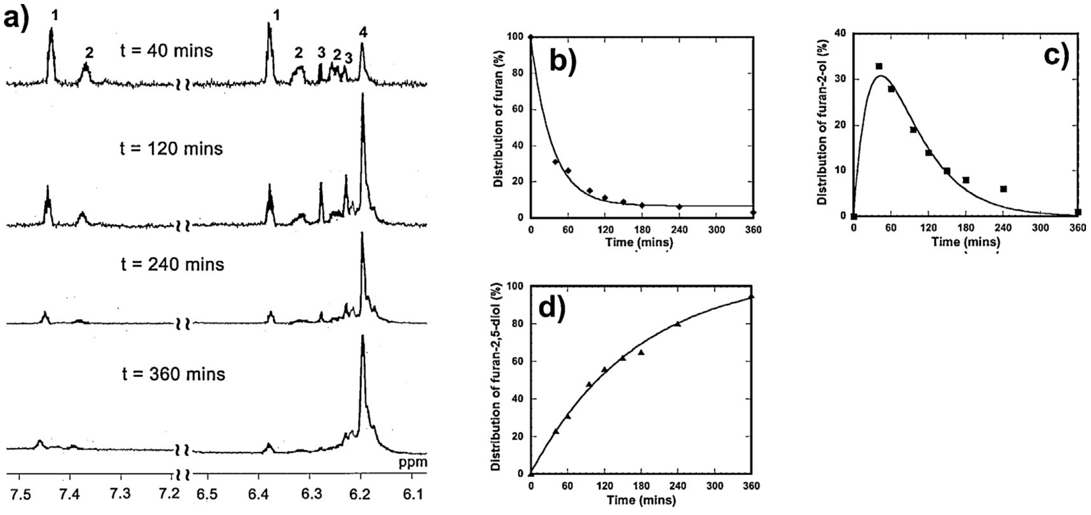


Fig. 4. (a) ^{1}H NMR traces showing the progress of the aerobic oxidation of furan in the presence of 1 equiv. HemiQ[6] in neutral conditions (pD = 6.3) (**1**: furan, **2**: furan-2-ol, **3**: intermediate, **4**: furan-2,5-diol), and the distribution plots of (b) furan, (c) furan-2-ol, and (d) furan-2,5-diol.

the host–guest interaction between HemiQ[6] and furan, but also the aerobic oxidation. Moreover, the crucial role of the proton is proved by independent experiments which show that when the HemiQ[6]-catalytic oxidation of furan is carried out in different organic solvents and basic aqueous solution, the same product, furan-2,5-diol, is observed in methanol after heating for 15 h (Fig. S7, ESI) but there is no reaction in either the aprotic solvent chloroform or an aqueous solution of Na_2CO_3 (pD = 10). The other members of the cucurbituril family, HemiQ[12], Q[6] and Q[7], have also been tested in this system, but no oxidation was observed, only the host–guest interaction between furan and Q[7] (Fig. S8, ESI). It is concluded that this supramolecular catalysis is dependent on the structure of the macrocyclic compound. To confirm the functionalization of HemiQ[6]'s cavity, imidazolidin-2-one has also been subjected but no observation of oxidation of furan.

From the experimental evidence for the host–guest interaction, as presented above, and the kinetic analysis of the aerobic oxidation of furan in the presence of HemiQ[6], a speculative mechanism has been established according to the aerobic oxidation of furan in ionic liquid (Scheme 3) [27]. This begins with the capture of a proton by HemiQ[6], which induces the formation of an inclusion complex between furan and HemiQ[6] with the protonation. Subsequently, an oxygen attacks to the α-carbon on furan, and the higher electronegativity of oxygen leads to an electron transfer from furan, to provide the hydroxyl group and produce furan-2-ol inside the HemiQ[6]. The intermediate includes closing of the second hydroxyl group and loosing of proton. Finally, the leaving of proton from the α-carbon provides the corresponding product, inclusion complex of furan-2,5-diol with HemiQ[6].

The substituted furan, 2-methylfuran, is also used in this HemiQ[6]-catalytic aerobic oxidation (Scheme 4). This is recorded with ^{1}H NMR, as shown in Figure 6a, while the proton resonances of the product 2-methylfuran-5-ol appear at δ 5.92 and δ 6.18 ppm. The conversion of the 2-methylfuran substrate has been non-linearly fitted to formula (4) and reveals that the kinetics follow first-order behavior, with $k_1 = 7.7 \times 10^{-2}\ \mathrm{min}^{-1}$ (Fig. 6b). This is about 3 times greater than for the oxidation of furan. The improved rate can be considered as a result of the relationship between the structure of 2-methylfuran and the electron distribution, namely, that there is higher electron density on the

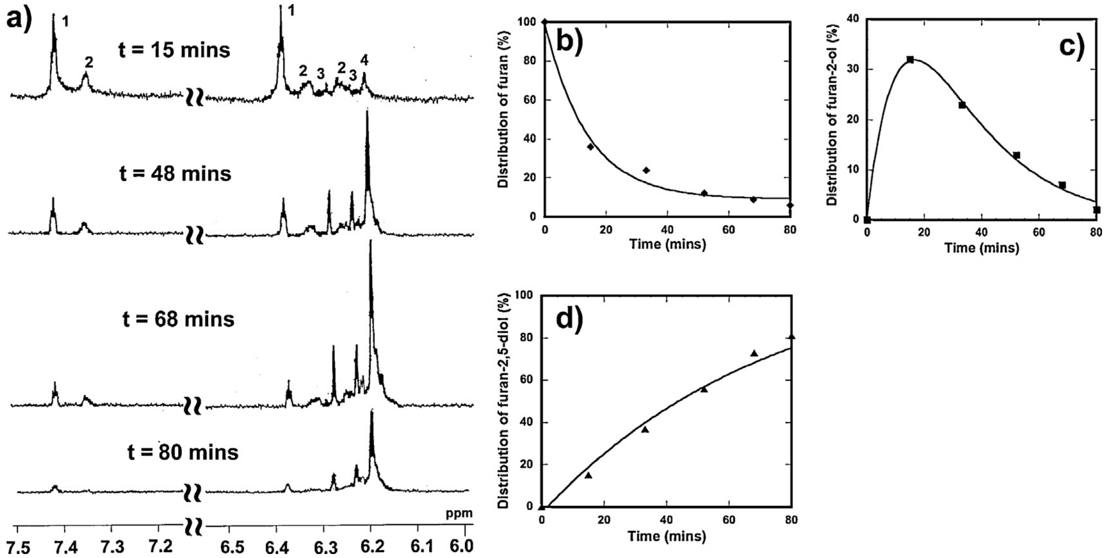
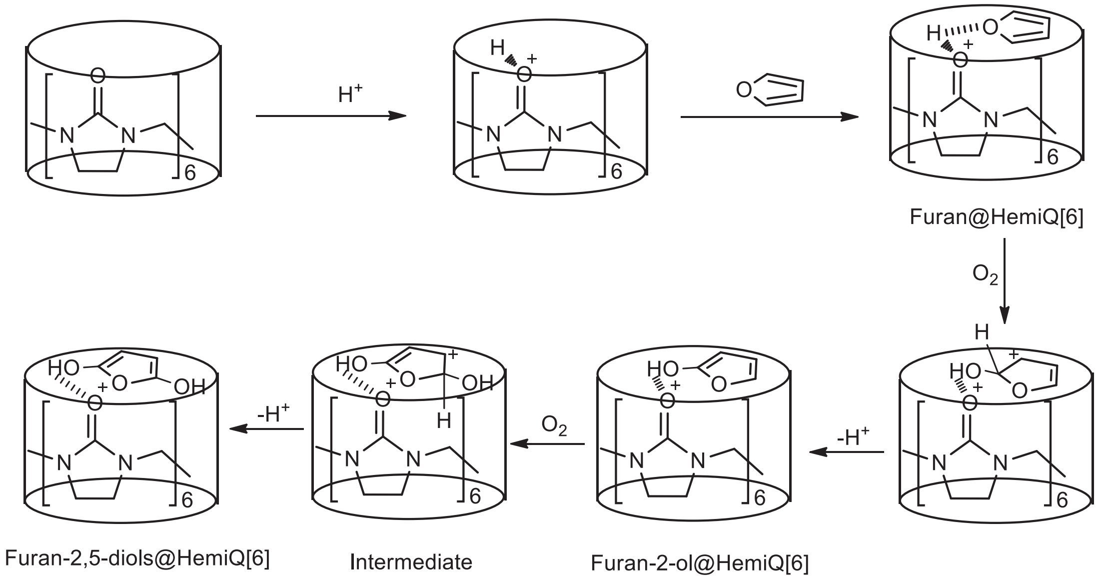
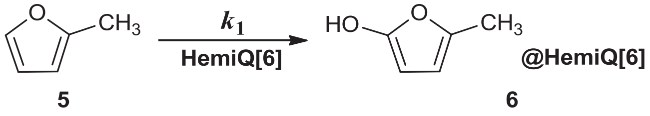


Fig. 5. (a) ^{1}H NMR traces showing the progress of the aerobic oxidation of furan in the presence of 1 equiv. HemiQ[6] in acid conditions (pD = 2) (**1**: furan, **2**: furan-2-ol, **3**: intermediate, **4**: furan-2,5-diol), and the distribution plots for (b) furan, (c) furan-2-ol, and (d) furan-2,5-diol.



Scheme 3. Possible pathway for the aerobic oxidation of furan in the presence of HemiQ[6].



Scheme 4. Oxidation of 2-methylfuran in the presence of HemiQ[6].

unsubstituted α-carbon of the substrate due to the presence of the electron donating methyl group. The oxidation of 2-methylfuran is too rapid in acid solution (pD = 2) to be traced and provide an exact kinetic constant, but it is confirmed that the oxidation is accelerated by the addition of the proton. The HemiQ[6]-catalytic aerobic oxidation products of 2-methylfuran was treated with DCl and neutralized with Na_2CO_3 followed by extraction with $CDCl_3$ same as that of furan. Interestingly, it was also found that the product 2-methylfuran-5-ol was tautomerized to 5-methyl-2(5*H*)-furanone [29] after the decomplexation with HemiQ[6] (Fig. S10). This result strongly supports the aerobic oxidation of 2-methylfuran does occur in the presence HemiQ[6] under the conditions used.

The oxidation of another five-member heterocyclic compound, thiophene, in the presence of HemiQ[6] (Scheme 5), proceeds very slowly in neutral conditions (Fig. 7a), and less than 5% of the product thiophene-2,5-diol was found after heating for 720 min. For this reason, the complete oxidation in this case may take a couple of days which makes it very difficult to describe the full kinetics. The initial rates of conversion of thiophene and the yield of thiophene-2,5-diol have been employed to estimate the kinetic properties, and the kinetic data have been linearly fitted to give the corresponding $k_1 = 4.1 \times 10^{-2}$ min^{-1} and $k_2 = 6.6 \times 10^{-3}$ min^{-1} (Fig. 7b and c). As in the case of the oxidation of furan, the secondary oxidation is slower than the initial step, and it is taken for granted that this is the rate-determining step in this procedure. On the other hand, the different activities between furan and thiophene could be considered to arise because the association of the sulfur on thiophene with the proton captured by HemiQ[6] is weaker than that in the case of furan.

The acceleration of the HemiQ[6]-induced oxidation of thiophene with the addition of a proton is also observed. In acidic conditions (pD = 2.0), the ^{1}H NMR trace indicates that the conversion is faster than that in neutral solution (Fig. 8a); the kinetic data have been fitted with initial rates of $k_1 = 8.9 \times 10^{-2}$ min^{-1} and $k_2 = 2.1 \times 10^{-2}$ min^{-1} (Fig. 8b and c). These have clearly been improved by 2 or 3 times upon acidification. Interestingly, the last

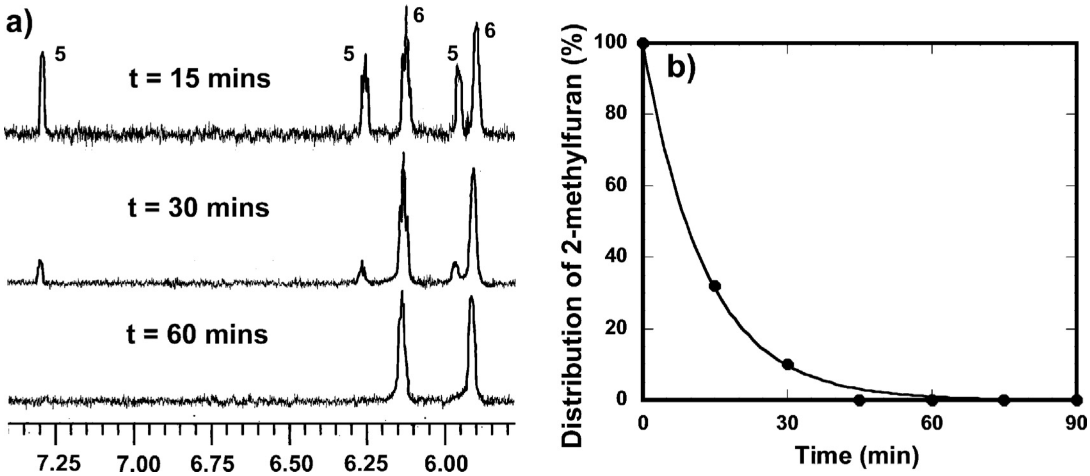
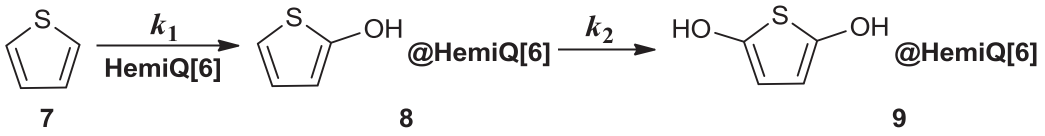


Fig. 6. (a) ^{1}H NMR traces showing progress of the aerobic oxidation of 2-methylfuran in the presence of 1 equiv. HemiQ[6] in neutral conditions (pD = 6.3) (**5**: 2-methylfuran, **6**: furan-2-methyl-5-ol); (b) the distribution plot for 2-methylfuran.



Scheme 5. Oxidation of thiophene in the presence of HemiQ[6].

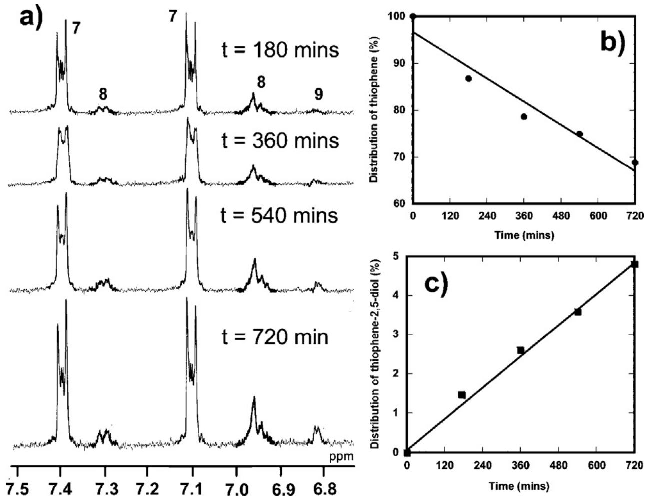


Fig. 7. (a) ^{1}H NMR traces showing progress of the aerobic oxidation of thiophene in the presence of 1 equiv. HemiQ[6] in neutral conditions (pD = 6.3) (**7**: thiophene, **8**: thiophene-2-ol, **9**: thiophene-2,5-diol), and the distribution plots for (b) thiophene and (c) thiophene-2,5-diol.

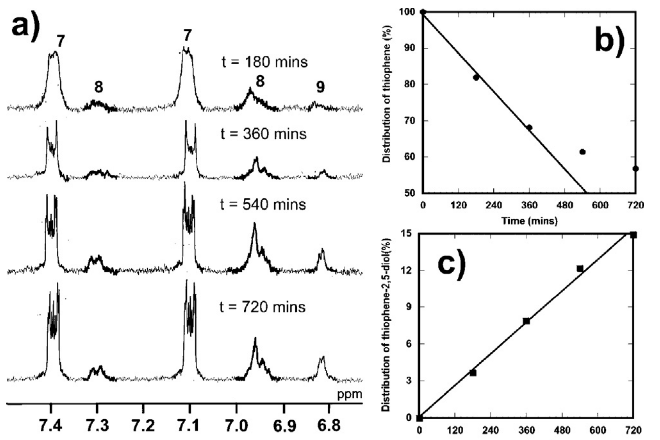


Fig. 8. (a) ^{1}H NMR traces showing progress of the aerobic oxidation of thiophene in the presence of 1 equiv. HemiQ[6] in acid conditions (pD = 2.0) (**7**: thiophene, **8**: thiophene-2-ol, **9**: thiophene-2,5-diol), and the distribution plots for (b) thiophene and (c) thiophene-2,5-diol.

two plots of thiophene conversion depart from the line of fit (Fig. 8b) due to the fact that the first oxidation of the substrate is resisted by the rate determining step, secondary oxidation, so it seems that the oxidation prefers thiophene-2-ol as product over thiophene-2,5-diol.

4. Conclusion

In summary, we have developed a novel aerobic oxidation system catalyzed by HemiQ[6] in water. As a model substrate, furan encapsulated within HemiQ[6], has been oxidized to form furan-2,5-diol regio-selectively. The supramolecular catalytic oxidation can be improved by acidification, due to the protonation of HemiQ[6]. According to analysis of the oxidation kinetics using a ^{1}H NMR trace, a plausible mechanism has been proposed, including the host–guest interaction between furan and the protonated HemiQ[6], the attack of oxygen molecule to α-carbon of binding furan, and the proton transfer to introduce the hydroxyl groups on to the furan ring. The HemiQ[6]-induced aerobic oxidation is also effective on the substrates of 2-methylfuran and thiophene.

The HemiQ[6]-catalytic oxidation of heterocyclic compounds in aqueous solution via a supramolecular strategy offers an alternative to aerobic oxidation with no participation by any metal cation. Furthermore, the unique ability of HemiQ[6] to capture protons could be applied to other acid-assisted chemical systems, giving the prospect of further revelations in cucurbituril chemistry.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2013.08.025.

References

[1] J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, J. Am. Chem. Soc. 122 (2000) 540–541.
[2] A. Day, A.P. Arnold, R.J. Blanch, B. Snushall, J. Org. Chem. 66 (2001) 8094–8100.
[3] E. Masson, X. Ling, R. Joseph, L. Kyeremeh-Mensah, X. Lu, RSC Adv. 2 (2012) 1213–1247.
[4] H. Cong, Z. Tao, S.-F. Xue, Q.-J. Zhu, Curr. Org. Chem. 15 (2011) 86–95.
[5] E.A. Karakhanov, L.M. Karapetyan, Y.S. Kardasheva, A.L. Maksimov, E.A. Runova, M.V. Terenina, T.Y. Filippova, Macromol. Symp. 270 (2008) 106–116.
[6] B.C. Pemberton, R. Raghunathan, S. Volla, J. Sivaguru, Chem. Eur. J. 18 (2012) 12178–12190.
[7] M.J. Pisani, Y. Zhao, L. Wallace, C.E. Woodward, F.R. Keene, A.I. Day, J.G. Collins, Dalton Trans. 39 (2010) 2078–2086.
[8] S. Kemp, N.J. Wheate, S. Wang, J.G. Collins, S.F. Ralph, A.I. Day, V.J. Higgins, J.R. Aldrich-Wright, J. Biol. Inorg. Chem. 12 (2007) 969–979.
[9] H. Cong, C.-R. Li, S.-F. Xue, Z. Tao, Q.-J. Zhu, G. Wei, Org. Biomol. Chem. 9 (2011) 1041–1046.
[10] M. Pattabiraman, A. Natarajan, R. Kaliappan, J.T. Mague, V. RamRamamurthy, Chem. Commun. (2005) 4542–4544.
[11] S.P. Gromov, A.I. Vedernikov, L.G. Kuzmina, D.V. Kondratuk, S.K. Sazonov, Y.A. Strelenko, M.V. Alfimov, J.A.K. Howard, Eur. J. Org. Chem. (2010) 2587–2599.
[12] B.C. Pemberton, N. Barooah, D.K. Srivatsava, J. Sivaguru, Chem. Commun. 46 (2010) 225–227.
[13] B.C. Pemberton, R.K. Singh, A.C. Johnson, S. Jockusch, S.J.P. Da, A. Ugrinov, N.J. Turro, D.K. Srivastava, J. Sivaguru, Chem. Commun. 47 (2011) 6323–6325.
[14] N. Basilio, L. Garcia-Rio, J.A. Moreira, M. Pessego, J. Org. Chem. 75 (2010) 848–855.
[15] N. Saleh, A.L. Koner, W.M. Nau, Angew. Chem. Int. Ed. 47 (2008) 5398–5401.
[16] H. Cong, F.-F. Zhao, J.-X. Jian, X. Zeng, Z. Tao, F.-X. Xue, Q.J. Zhu, Catal. Commun. 11 (2009) 167–170.
[17] Y.-H. Wang, H. Cong, F.-F. Zhao, S.-F. Xue, Z. Tao, Q.-J. Zhu, G. Wei, Catal. Commun. 12 (2011) 1127–1130.
[18] Y. Miyahara, K. Goto, M. Oka, T. Inazu, Angew. Chem. Int. Ed. 43 (2004) 5019–5022.
[19] H. Cong, T. Yamato, X. Feng, Z. Tao, J. Mol. Catal. A: Chem. 365 (2012) 181–185.
[20] C. Parmeggiani, F. Cardona, Green Chem. 14 (2012) 547–564.

[21] Y. Endo, J.-E. Bäckvall, Chem. Eur. J. 17 (2011) 12596–12601.
[22] I.E. Markó, A. Gautier, R. Dumeunier, K. Doda, F. Philippart, S.M. Brown, C.J. Urch, Angew. Chem. Int. Ed. 43 (2004) 1588–1591.
[23] G.G. Melikyan, Synthesis (1993) 833–850.
[24] S.S. Stahl, Science 309 (2005) 1824–1826.
[25] B. Guan, D. Xing, G. Cai, X. Wan, N. Yu, Z. Fang, L. Yang, Z. Shi, J. Am. Chem. Soc. 127 (2005) 18004–18005.
[26] D.C. Spellmeyer, K.N. Houk, N.G. Rondan, R.D. Miller, L. Franz, G.N. Fickes, J. Am. Chem. Soc. 111 (1989) 5356–5367.
[27] O.A. Fall, M. Sène, E. Tojo, G. Gómez, Y. Fall, Synthesis 20 (2010) 3415–3417.
[28] G.-L. Zhang, Z.-Q. Xu, S.-F. Xue, Q.-J. Zhu, Z. Tao, Chin. J. Inorg. Chem. 19 (2003) 655–659.
[29] S.-R. Sheng, L. Xu, X.-L. Zhang, X.-L. Liu, M.-H. Wei, J. Comb. Chem. 8 (2006) 805–807.