ELECTRONIC SUPPLEMENTARY INFORMATION

Guest-adjusted encapsulations and Thermal Studies of Non-porous Mononuclear Cu(II) Coordination Complexes through Electrostatic Interactions Induced by Fluorine Substitutions

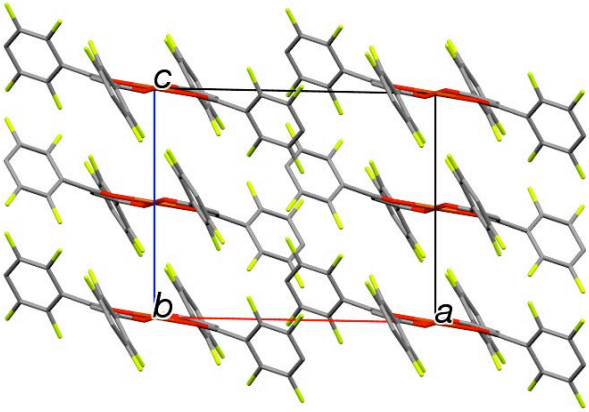
A. Hori,* K. Nakajima, Y. Akimoto, K. Naganuma, H. Yuge
*To whom the correspondence should be addressed (e-mail: hori@kitasato-u.ac.jp)

---

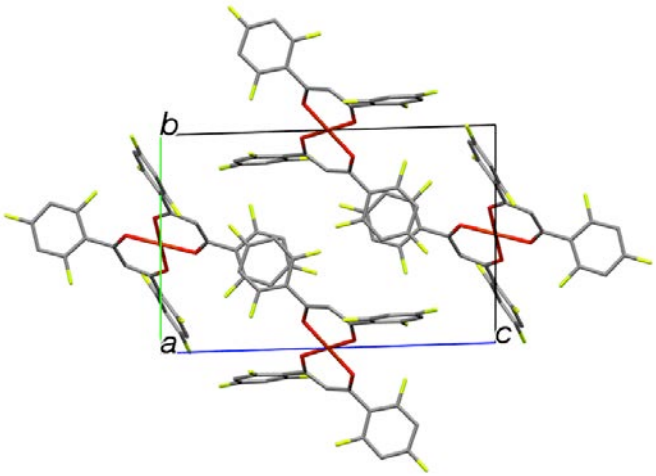
1. Packing structures of the Cu^{2+} complexes 2, 3a, and 4a.

Single component crystals of **2**, **3a**, and **4a** were obtained from EtOH, CH_2Cl_2, and $CHCl_3$ without guests. With unencapsulated guests, *e.g.*, durene (**12**), the single-component complex and the guest were separately crystallized from the solution mentioned above. No single component crystals of **1** unfortunately obtained in our experiments, and only the crystal of **1**•$(H_2O)_4$ were crystallized in CH_2Cl_2, $CHCl_3$, $CHCl_3$-hexane, etc.

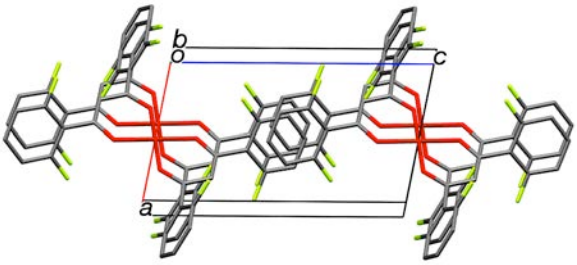
a) **2** ($C_{30}H_6CuF_{16}O_4$: *Mw* = 797.90): monoclinic, $P2_1/c$



b) **3a** ($C_{30}H_{10}CuF_{12}O_4$: *Mw* = 725.93): triclinic, *P*-1



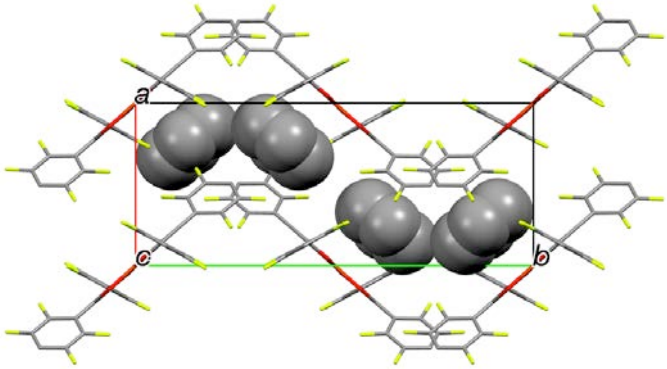
c) **4a** ($C_{30}H_{14}CuF_8O_4$: *Mw* = 653.96): triclinic, *P*-1



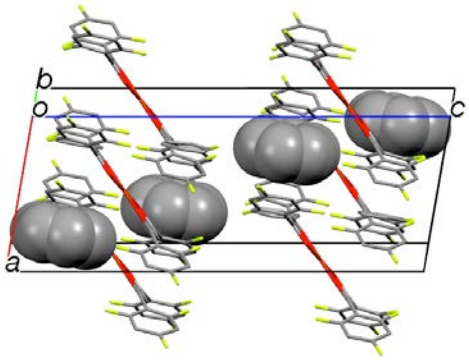
2. Packing structures of 2 and 3a with 6.

The benzene encapsulated crystals **2**•(**6**)$_2$ and **3a**•(**6**)$_2$ were obtained from CH_2Cl_2-benzene. The information of the single crystal of **1**•(**6**)$_2$ was summarized in ref. 16 (Hori & Arii, *CrystEngComm*, **2007**, *9*, 215-217).

a) **2**•(**6**)$_2$ ($C_{42}H_{18}CuF_{16}O_4$: *Mw* = 954.11): monoclinic, $P2_1/c$



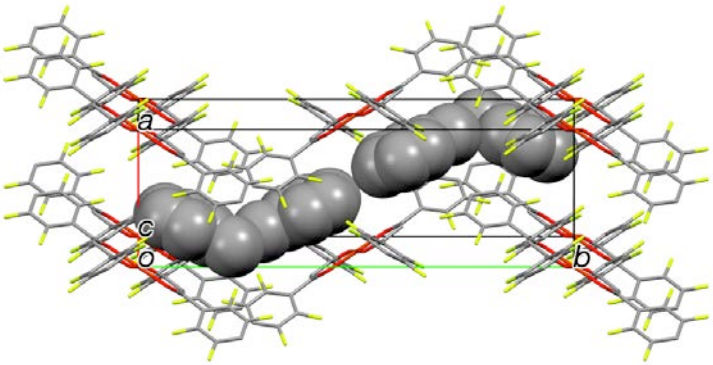
b) **3a**•(**6**)$_2$ ($C_{42}H_{22}CuF_{12}O_4$: *Mw* = 882.15): monoclinic, $C2/c$



3. Packing structure of 2 with 7.

The toluene encapsulated crystal **2**•(**7**)$_4$ was obtained from toluene.

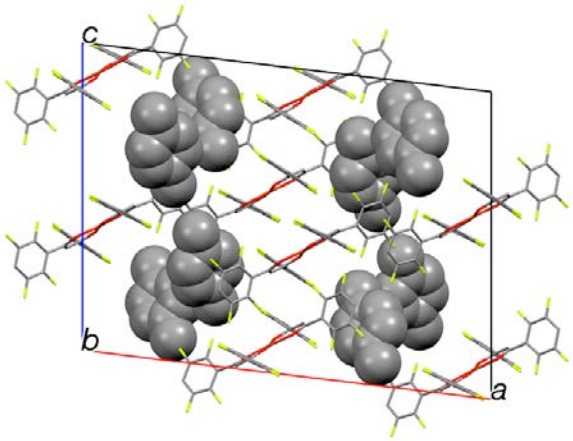
2•(**7**)$_2$ ($C_{44}H_{22}CuF_{16}O_4$: *Mw* = 982.17): monoclinic, $P2_1/c$



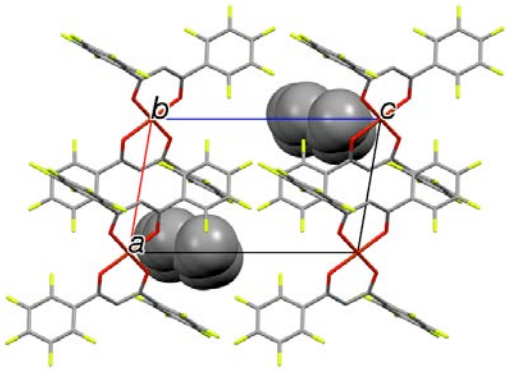
4. Packing structures of 1, 2, and 3a·with 8.

The p-xylene encapsulated crystal **1**•**8** was obtained from p-xylene-EtOH. The crystals **1**•(**8**)$_2$ and **1**•(**8**)$_4$ was obtained in a p-xylene-CH_2Cl_2. The information of the three crystals is currently summarized and submitted. The crystals **2**•**8** and **3a**•**8** were obtained from corresponding xylene-CH_2Cl_2.

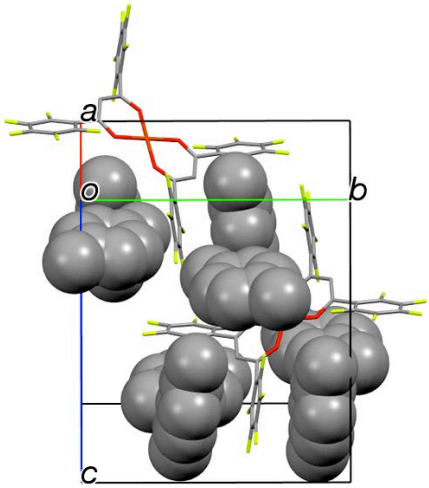
a) **1**•**8** ($C_{38}H_{12}CuF_{20}O_4$: *Mw* = 976.03): orthorhombic, *P*bca



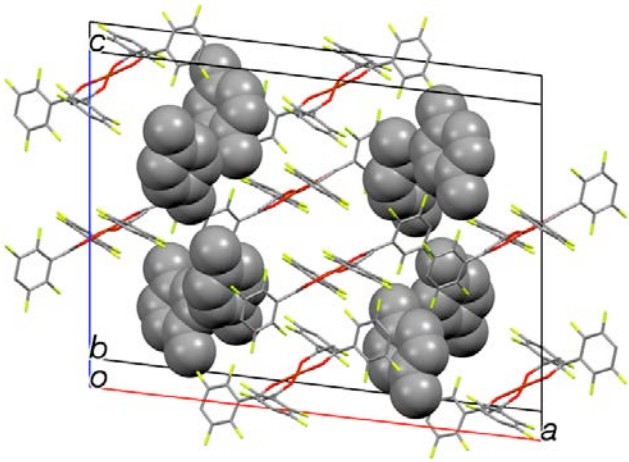
b) **1**•(**8**)$_2$ ($C_{46}H_{22}CuF_{20}O_4$: *Mw* = 1082.19): triclinic, *P*-1



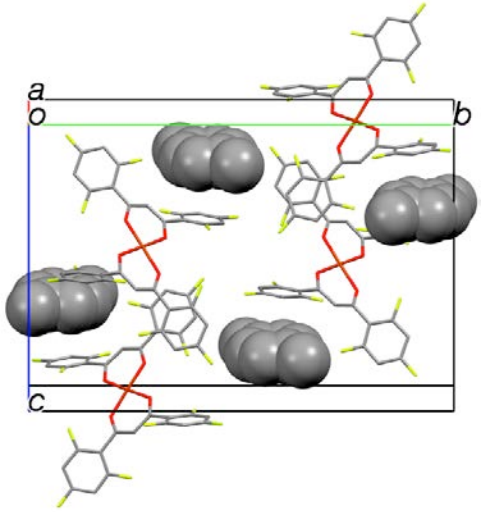
c) **1•(8)**$_4$ ($C_{62}H_{42}CuF_{20}O_4$: *Mw* = 1294.51): monoclinic, P_n



d) **2•8** ($C_{38}H_{16}CuF_{16}O_4$: *Mw* = 904.06): monoclinic, *C*2/c



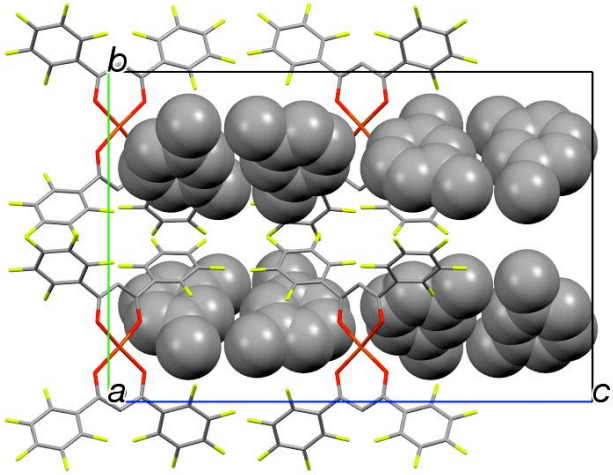
e) **3a•8** ($C_{38}H_{20}CuF_{12}O_4$: *Mw* = 832.09): monoclinic, $P2_1/c$



5. Packing structure of 1·with 9.

The m-xylene encapsulated crystal **1•(9)**$_2$ was obtained from m-xylene-CH_2Cl_2.

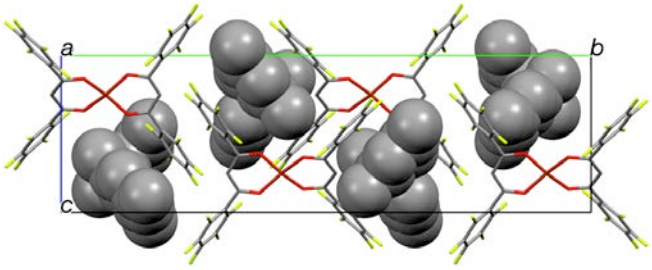
1•(9)$_2$ ($C_{48}H_{26}CuF_{20}O_4$: *Mw* = 1110.23): orthorhombic, $Pca2_1$



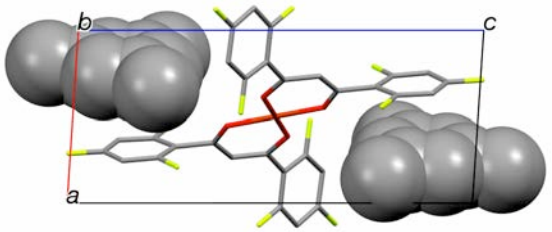
6. Packing structures of 1·and 3a with 11.

The mesitylene encapsulated crystals **1•(11)**$_2$ and **3a•(11)**$_2$ were obtained from mesitylene-CH_2Cl_2.

a) **1•(11)**$_2$ ($C_{48}H_{26}CuF_{20}O_4$: *Mw* = 1110.23): monoclinic, *C*2/c



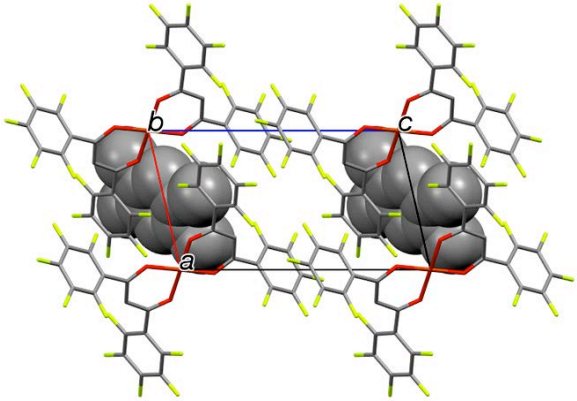
b) **3a•(11)**$_2$ ($C_{48}H_{34}CuF_{12}O_4$: *Mw* = 966.30): triclinic, *P*-1



7. Packing structure of 1·with 12.

The durene encapsulated crystal **1•12** was obtained from durene-CH_2Cl_2. Each CH_2Cl_2 solution of durene with **2** and **3a** produces the single-component crystals of **2** and **3a**, respectively.

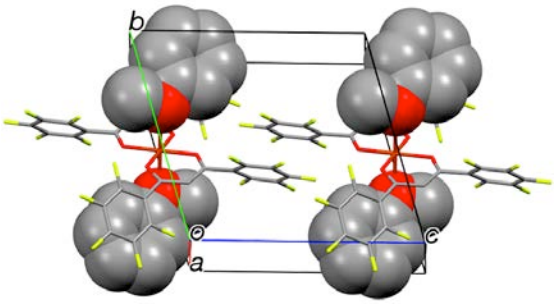
1•12 ($C_{40}H_{16}CuF_{20}O_4$: *Mw* = 1004.08): triclinic, *P*-1



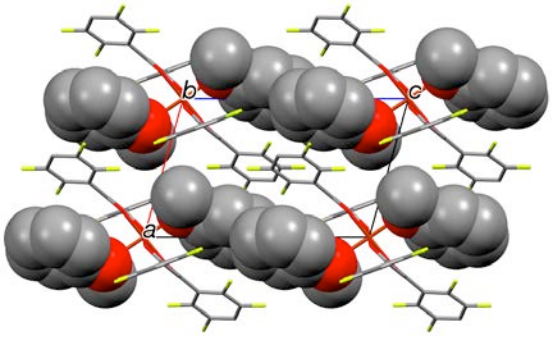
8. Packing structures of 1, 2, and 3a·with 13.

The anisole encapsulated crystals **1•(13)**$_2$, **2•(13)**$_2$, and **3a•(13)**$_2$ were obtained from anisole-CH_2Cl_2.

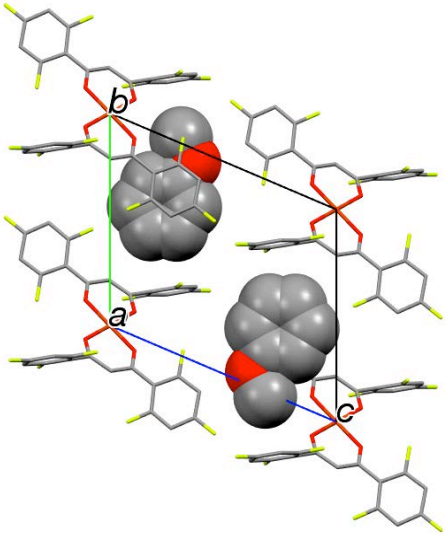
a) **1•(13)**$_2$ ($C_{44}H_{18}CuF_{20}O_6$: *Mw* = 1086.13): triclinic, *P*-1



2•(13)$_2$ ($C_{44}H_{22}CuF_{16}O_6$: *Mw* = 1014.17): triclinic, *P*-1



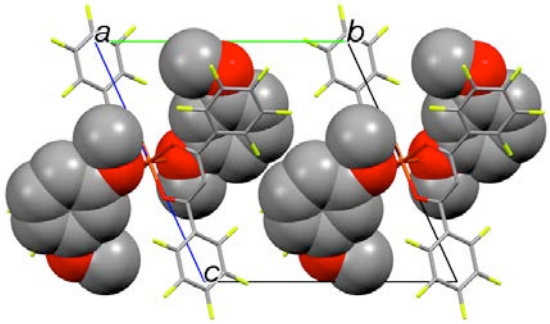
3a•(13)$_2$ ($C_{44}H_{26}CuF_{12}O_6$: *Mw* = 942.20): triclinic, *P*-1



9. Packing structures of 1 with 14.

The 1,3-dimethoxybenzene encapsulated crystal **1**•(**14**)$_2$ was obtained from 1,3-dimethoxybenzene-CH_2Cl_2. Each CH_2Cl_2 solution of 1,3-dimethoxybenzene with **2** and **3a** produces the single-component crystals of **2** and **3a**, respectively.

1•(**14**)$_2$ ($C_{46}H_{22}CuF_{20}O_8$: *Mw* = 1146.19): triclinic, *P*-1



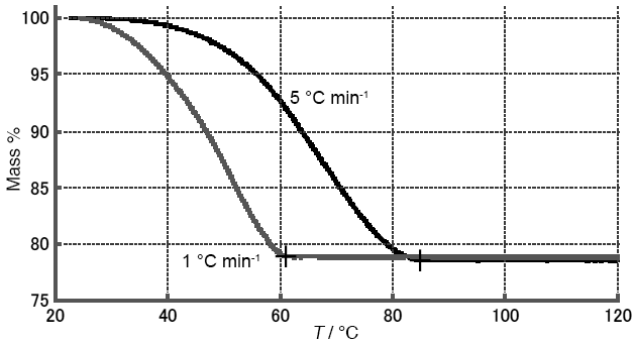
10. Summary of the mainly contributed interactions in the crystals.

crystals	arene-perfluoroarene	$Cu^{2+}\cdots\pi$	$Cu^{2+}\cdots F$	another remarkable interactions
1•(**6**)$_3$ (ref. 16)	exist	exist (3.42 Å)	no	CF···HC, CF···π_{C6F5}
2•(**6**)$_2$	no	exist (3.39 Å)	no	CH···π, CF···HC
3•(**6**)$_2$	no	possible (4.16 Å)	no	CF···HC
2•(**7**)$_2$	no	exist (3.44 Å)	no	
1•**8** (ref. 28)	exist (3.47 Å)	no	possible (2.83 Å)	CF···HC
1•(**8**)$_2$ (ref. 28)	possible (3.76 Å)	no	possible (2.98 Å)	CF···π_{C6F5}
1•(**8**)$_4$ (ref. 28)	exist (3.56 Å)	possible (3.75 Å)	no	
2•**8**	possible (3.72 Å)	no	possible (2.71 Å)	CF···HC, $\pi_{C6F4H}\cdots\pi_{C6F4H}$
3•**8**	possible (3.70 Å)	no	possible (2.78 Å)	CF···HC
1•(**9**)$_2$	exist (3.53 Å)	no	possible (2.82 Å)	
1•(**11**)$_2$	possible (3.60 Å)	no	possible (2.82 Å)	CF···π_{C6F5}
3•(**11**)$_2$	possible (3.75 Å)	no	exist (2.63 Å)	
1•**12**	exist (3.47 Å)	no	possible (3.21 Å)	CF···FC
1•(**13**)$_2$	possible (3.76 Å)	no	no	$Cu^{2+}\cdots$O, CF···HC
2•(**13**)$_2$	possible (3.63 Å)	no	no	$Cu^{2+}\cdots$O, $\pi_{C6F4H}\cdots\pi_{C6F4H}$
3•(**13**)$_2$	possible (3.71 Å)	no	possible (2.78 Å)	CF···HC
1•(**14**)$_2$	possible (3.66 Å)	no	no	$Cu^{2+}\cdots$O, CF···FC

The shortest distance was shown for each crystals.

11. TG curves of 1•(6)$_3$ at the scanning rates 5 and 1 °C min^{-1}

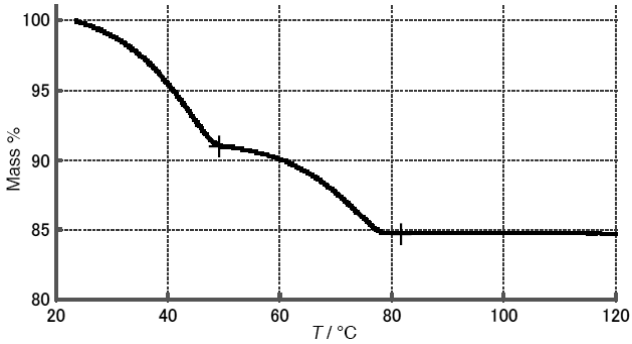
The temperature of the guest release depended on the scanning rates, and the TG curve of **1**•(**6**)$_3$ in the conditions of 1 °C min^{-1} shows the guest releases around rt~60 °C. All the TG results in this article are shown at the same scanning rate, 5 °C min^{-1}, for the comparison.



12. The guest encapsulation of powder samples 1, 2, and 3a.

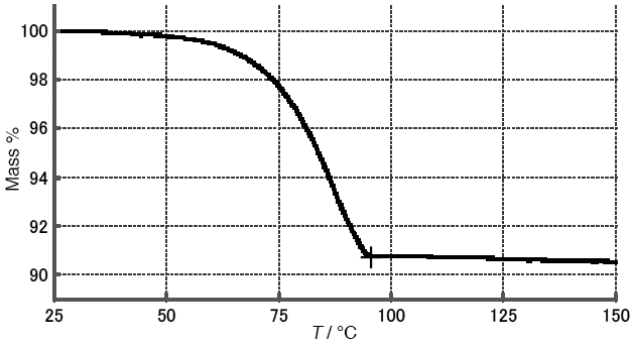
The appearance of the samples and TG results were summarized: the powder of complex **1** encapsulated guest molecules, benzene and toluene, but no encapsulations of the guests were observed in the powder of **2** or **3a**.

a) **1** (powder) -- benzene diffusion --> **1**•(**6**)$_3$ --> **1**



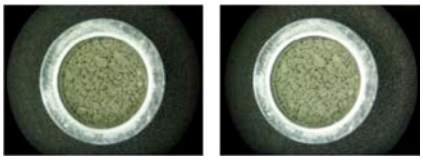
Benzene release: 23.6 °C (100wt%), 49.2 °C (91.0wt%), 78.7 °C (84.8wt%)

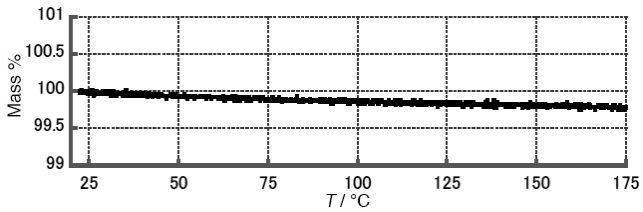
b) **1** (powder) -- toluene diffusion --> **1**•**7** --> **1**



Toluene release: 46.5 °C (99.9wt%), 95.9 °C (90.8wt%)

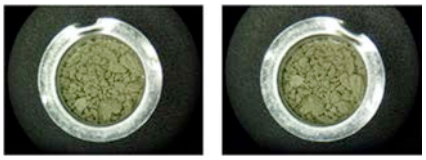
c) **2** (powder) -- benzene diffusion --> **2**

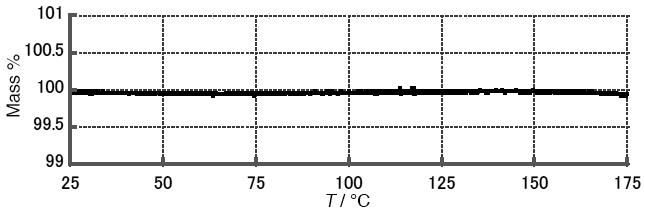




Benzene release: no guest releases was observed.

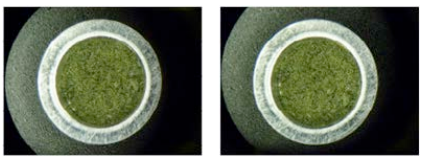
d) **2** (powder) -- toluene diffusion --> **2**

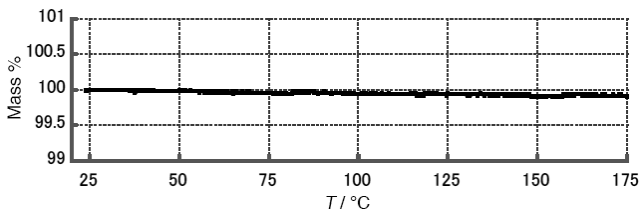




Toluene release: no guest releases was observed.

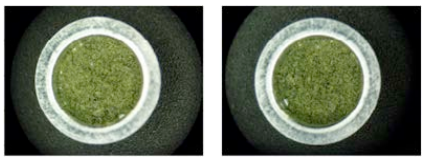
e) **3a** (powder) -- benzene diffusion --> **3a**

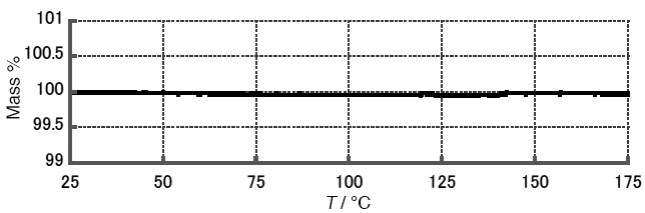




Benzene release: no guest releases was observed.

f) **3a** (powder) -- toluene diffusion --> **3a**



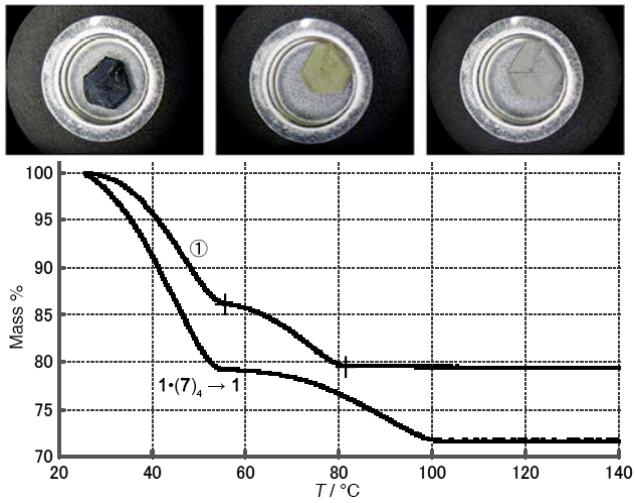


Toluene release: no guest releases was observed.

13. Overviews and TG curves of the starting crystals and their benzene encapsulated crystals.

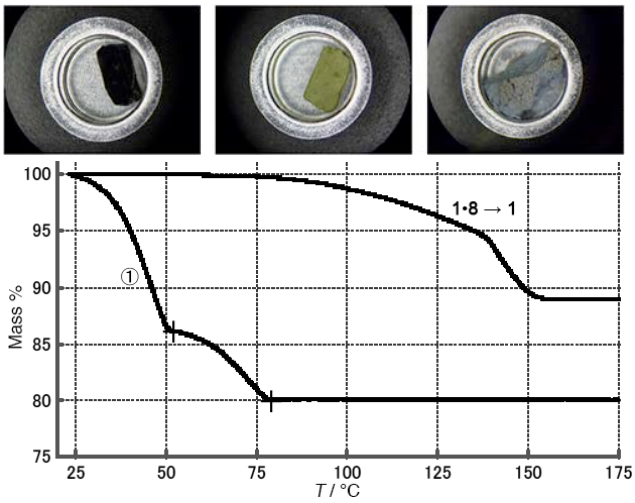
TG curves of benzene release (1) are shown with the TG curves of the starting crystals. The calculated value of the weight percent of **1** in **1**•(**6**)$_3$ is 78.8 wt%, and the experimental results show good agreements with the calculation values.

a) **1**•(**7**)$_4$ --> **1** --> **1**•(**6**)$_3$



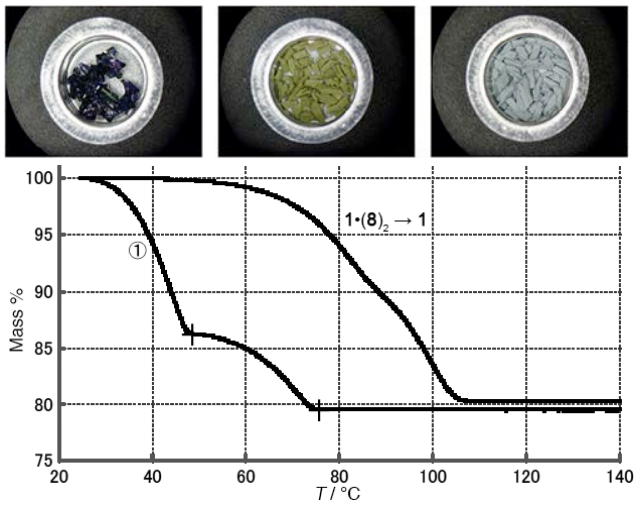
Benzene release: 26.3 °C (100wt%), 55.4 °C (86.2wt%), 81.7 °C (79.5wt%)

b-1) **1**•**8** --> **1** --> **1**•(**6**)$_3$



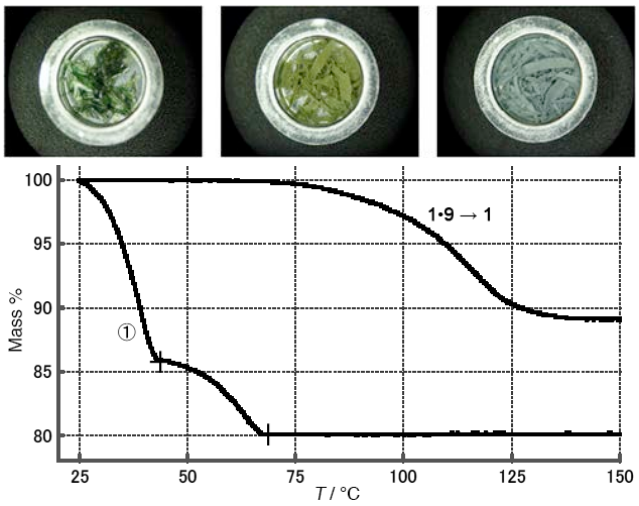
Benzene release: 24.8 °C (100wt%), 53.4 °C (85.8wt%), 79.2 °C (80.0wt%)

b-2) **1**•(**8**)$_2$ --> **1** --> **1**•(**6**)$_3$



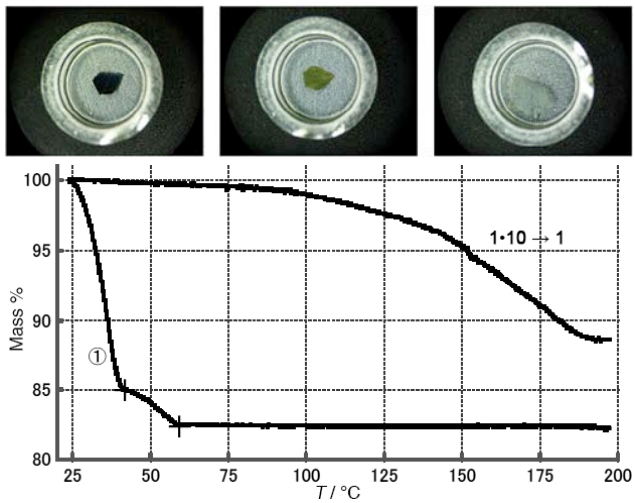
Benzene release: 25.9 °C (100wt%), 47.8 °C (86.4wt%), 75.3 °C (79.5wt%)

c) **1**•(**9**)$_2$ --> **1** --> **1**•(**6**)$_3$



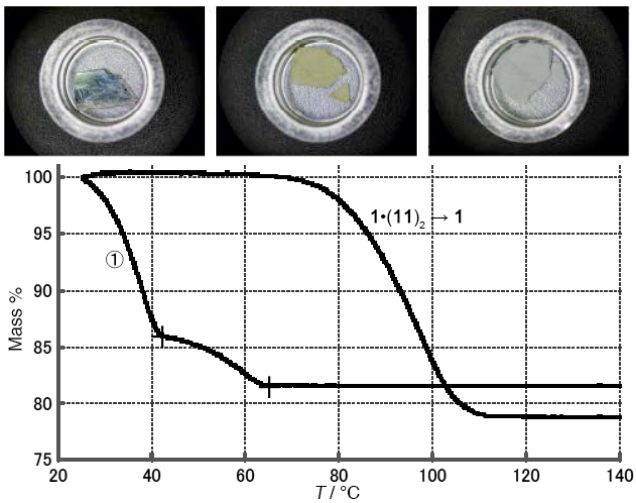
Benzene release: 24.6 °C (100wt%), 43.0 °C (86.0wt%), 68.0 °C (80.1wt%)

d) **1**•**10** --> **1** --> **1**•(**6**)$_3$



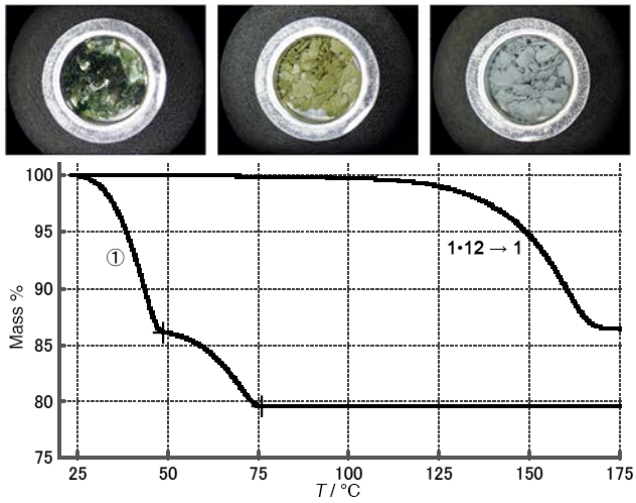
Benzene release: 25.1 °C (99.9wt%), 40.9 °C (85.2wt%), 59.1 °C (82.6wt%)

e) **1**•(**11**)$_2$ --> **1** --> **1**•(**6**)$_3$



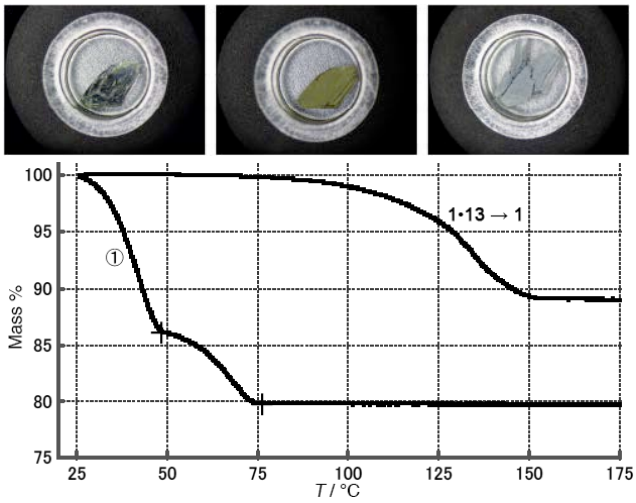
Benzene release: 26.6 °C (99.8wt%), 42.2 °C (86.0wt%), 64.6 °C (81.6wt%)

f) **1•12** --> **1** --> **1•(6)**$_3$



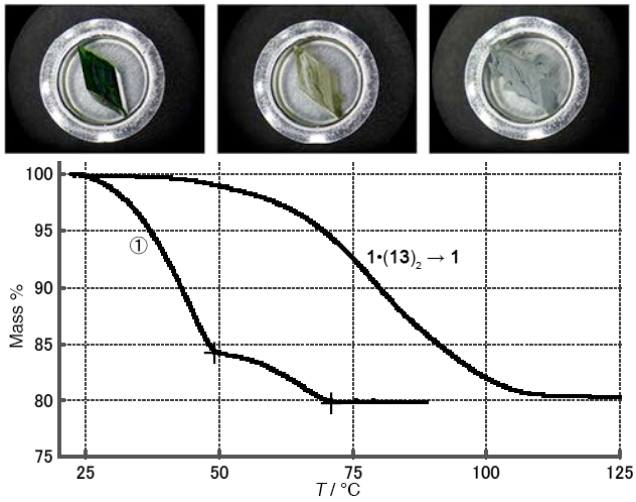
Benzene release: 25.0 °C (100wt%), 48.2 °C (86.2wt%), 75.5 °C (79.6wt%)

g-1) **1•13** --> **1** --> **1•(6)**$_3$



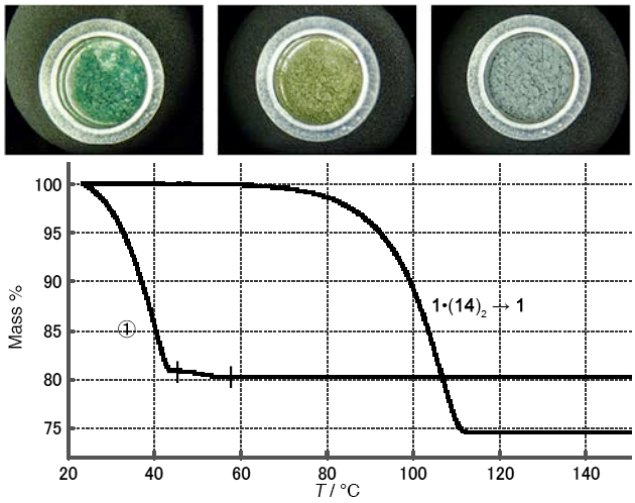
Benzene release: 24.6 °C (100wt%), 48.6 °C (86.2wt%), 75.5 °C (79.9wt%)

g-2) **1•(13)**$_2$ --> **1** --> **1•(6)**$_3$



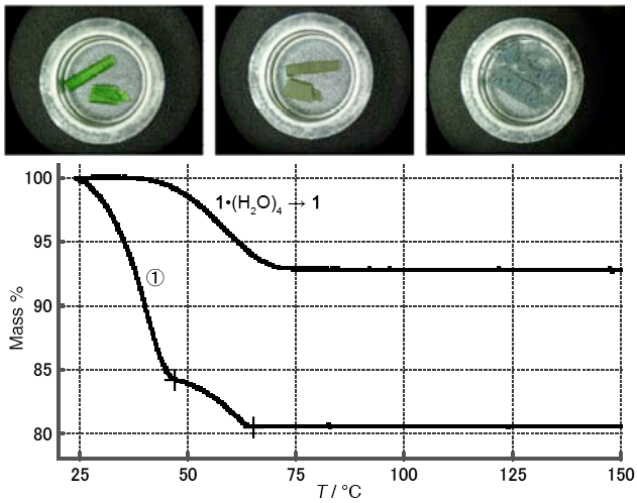
Benzene release: 23.4 °C (100wt%), 49.4 °C (84.3wt%), 70.7 °C (80.0 wt%)

h) **1•(14)**$_2$ --> **1** --> **1•(6)**$_3$



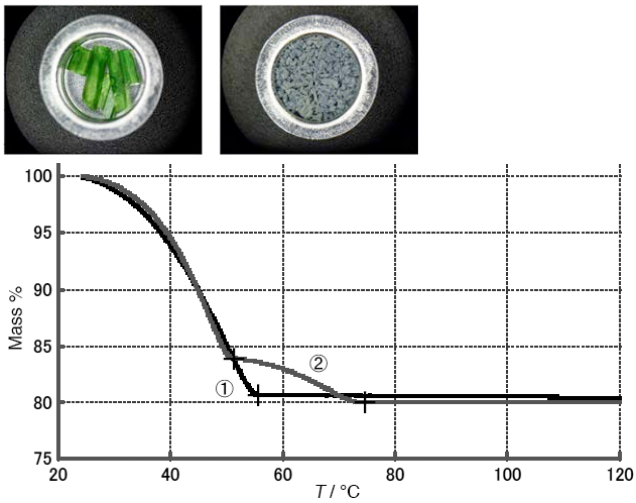
Benzene release: 26.7 °C (99.9wt%), 46.5 °C (81wt%), 57.8 °C (80.3wt%)

i-1) **1•**$(H_2O)_4$ --> **1** --> **1•(6)**$_3$



Benzene release: 24.4 °C (99.9wt%), 46.3 °C (84.9wt%), 64.4 °C (80.6 wt%)

i-2) **1•**$(H_2O)_4$ --> **1•(6)**$_3$ (direct exchange reaction)

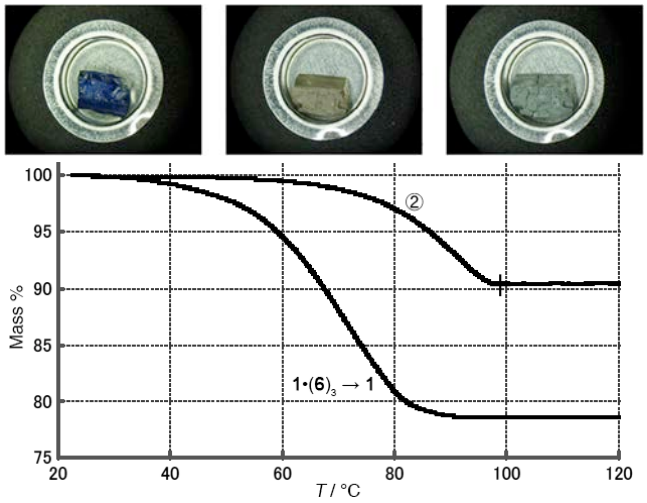


Benzene release: 1st) 24.4 °C (100wt%), 55.9 °C (80.6wt%)
2nd) 25.1 °C (100wt%), 50.9 °C (84.0wt%), 73.4 °C (80.0wt%)

14. Overviews and TG curves of the starting crystals and their toluene encapsulated crystals.

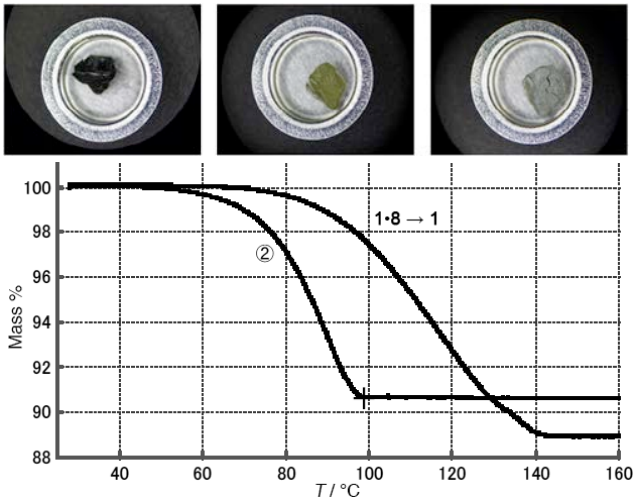
TG curves of the toluene release (2) are shown on the TG curves of the starting crystals. The calculated value of the weight percent of **1** in **1•7** is 90.4wt%, and the experimental results show good agreements with the calculation values.

a) **1•(6)**$_3$ --> **1** --> **1•7**



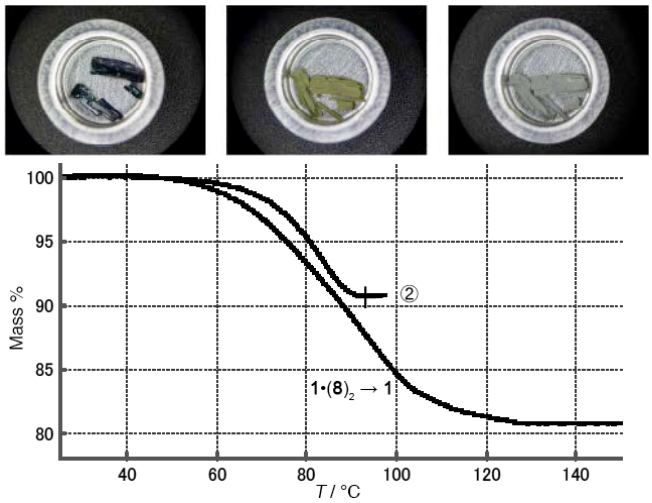
Toluene release: 59.8 °C (99.5wt%), 98.5 °C (90.4wt%)

b-1) **1•8** --> **1** --> **1•7**



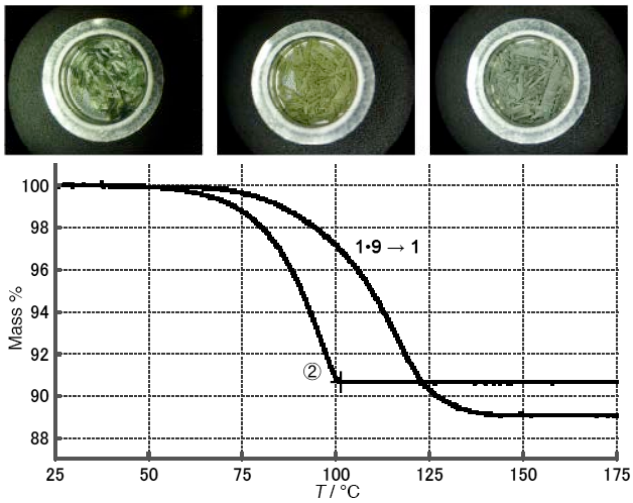
Toluene release: 49.0 °C (100.0 wt%), 98.6 °C (90.7wt%)

b-2) **1•(8)**$_2$ --> **1** --> **1•7**



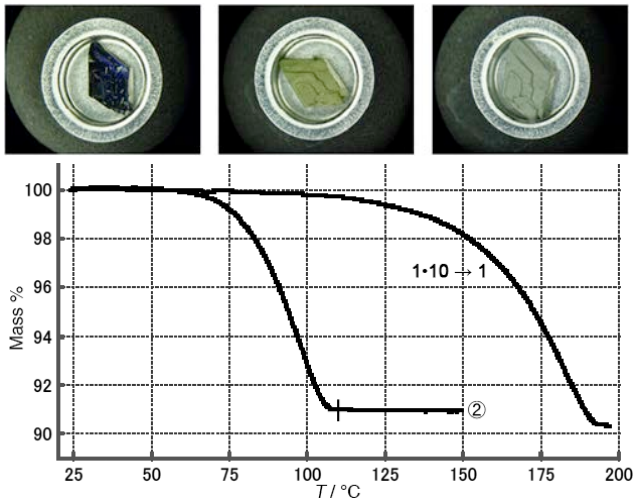
Toluene release: 56.7 °C (99.7wt%), 92.8 °C (90.8wt%)

c) **1•9** --> **1** --> **1•7**



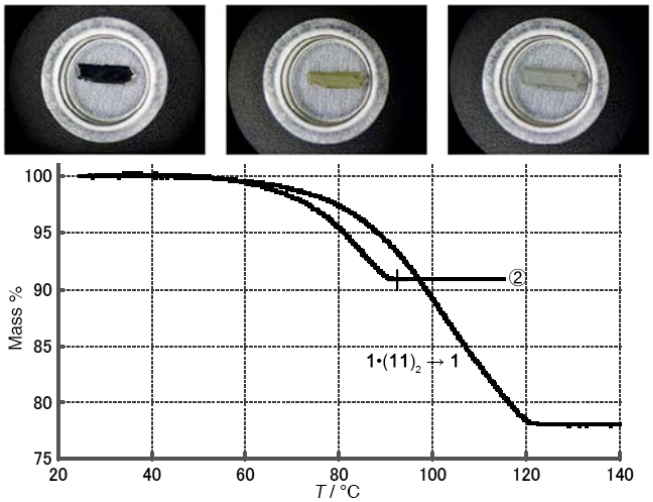
Toluene release: 56.3 °C (99.9wt%), 101.1 °C (90.7wt%)

d) **1•10** --> **1** --> **1•7**



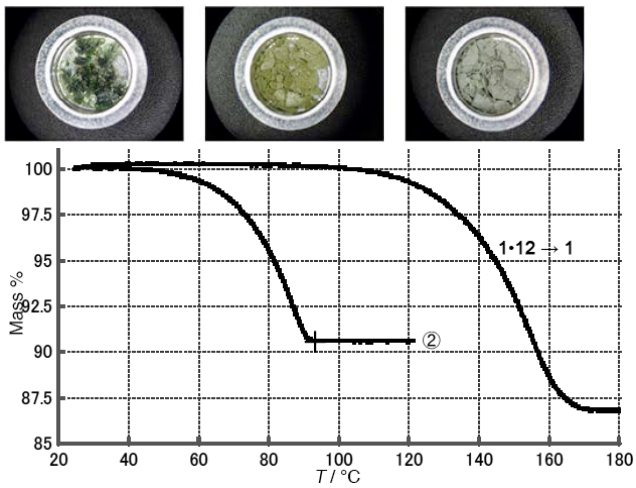
Toluene release: 61.7 °C (99.9 wt%), 108.4 °C (91.1wt%)

e) **1•(11)**$_2$ --> **1** --> **1•7**



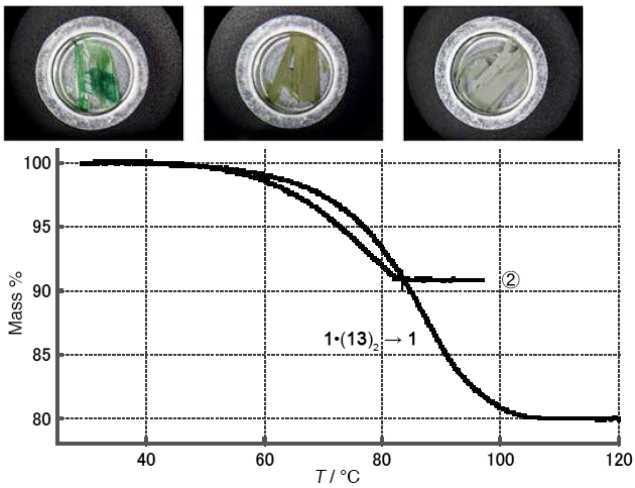
Toluene release: 53.8 °C (99.9wt%), 92.1 °C (90.9wt%)

f) **1•12** --> **1** --> **1•7**



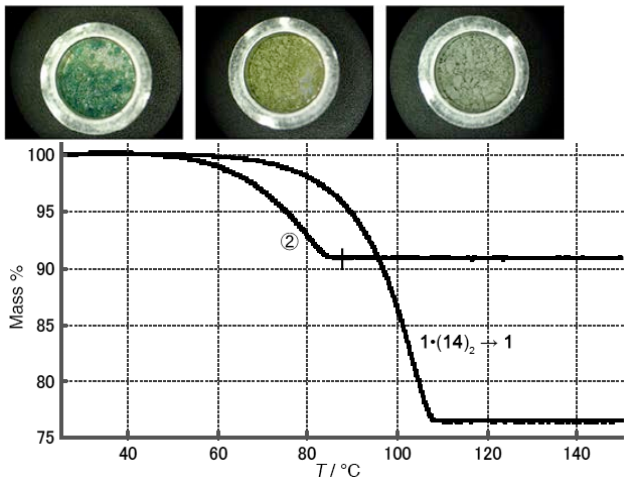
Toluene release: 50.5 °C (99.8 wt%), 92.6 °C (90.6wt%)

g) **1•(13)**$_2$ --> **1** --> **1•7**



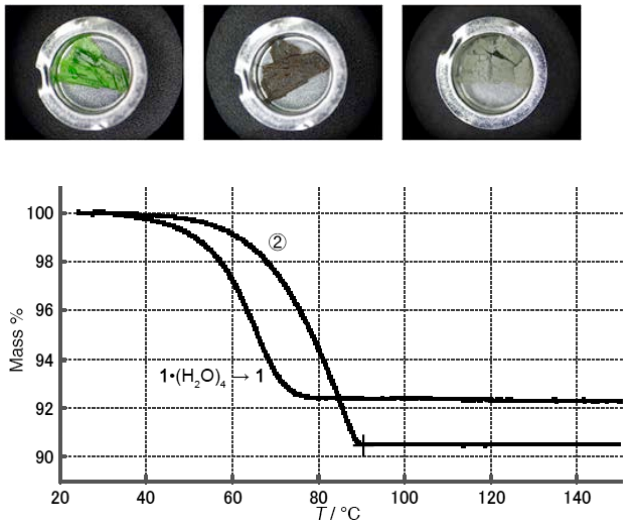
Toluene release: 46.6 °C (99.9 wt%), 83.8 °C (90.9wt%)

h) **1•(14)**$_2$ --> **1** --> **1•7**



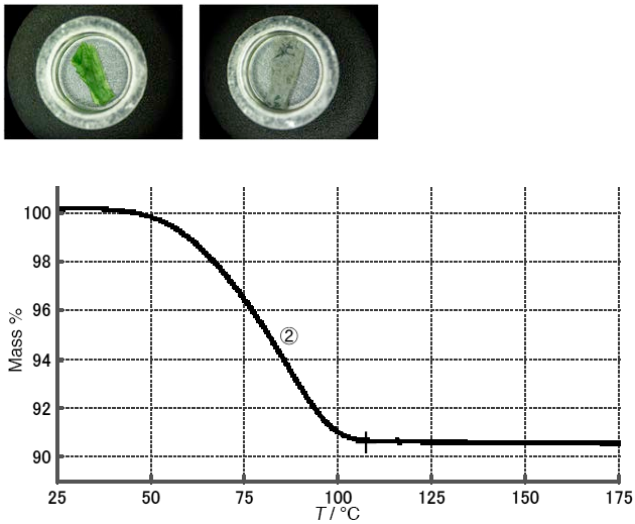
Toluene release: 49.5 °C (100wt%), 84.6 °C (91.1wt%)

i-1) **1•**(H_2O)$_4$ --> **1** --> **1•7**



Toluene release: 49.2 °C (99.7wt%), 89.7 °C (90.6wt%)

i-2) **1•**(H_2O)$_4$ --> **1•7** (direct exchange reaction)



Toluene release: 46.7 °C (100wt%), 108.0 °C (90.7wt%)