Supporting Information

Controlled deposition number of organic molecules using quartz crystal microbalance evaluated by STM single molecule counting

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Molecules used for QCM performance check

The performance of our home-build molecular evaporator and QCM were experimentally confirmed. In the experiment, two different phthalocyanine molecules [metal-free phthalocyanine (H₂Pc), and iron phthalocyanine (FePc)] and six different porphyrin molecules [metal-free tetraphenylporphyrin (H₂TPP), tetrakis(pentafluorophenyl)porphyrin (H₂TPFPP), tetrakis (di-tert-butylphenyl)porphyrin (H₂TTBPP), tetraphenylporphyrin iron(III) chloride (FeTPPCl), tetrakis(pentafluorophenyl)porphyrin iron(III) chloride (FeTPFPCl), and tetrakis(di-tert-butylphenyl)porphyrin iron(III) chloride (FeTPFPPCl), and tetrakis(di-tert-butylphenyl)porphyrin iron(III) chloride (FeTPFPPCl)] were sublimated with several crucible temperature, and measured their evaporation rates using QCM. Figure S1 shows the chemical structures of the molecules we used in the experiments. H₂Pc, H₂TPP, H₂TPFPP, and H₂TTBPP are metal-free molecules, while FePc, FeTPPCl, FeTPFPPCl, and FeTTBPPCl include Fe atom at the core.



Figure S1: Chemical structures of the two different phthalocyanine (H_2Pc , and FePc) and porphyrin (H_2TPP , H_2TPFPP , H_2TTBPP , FeTPPC1, FeTPFPPC1, and FeTTBPPC1) molecules we used in the experiment.

Monitoring QCM resonant frequency during molecular sublimation

Figure S2(a) presents typical result, showing time dependence of QCM resonant frequency (f) measured during the sublimation of H₂TPFPP molecules. The crucible temperature was increased by about every 10 min. At each temperature, f was decreased linearly with time under the equilibrium conditions [indicated by arrows in Fig. S2(a)]. One can see that the decrement rate of f becomes larger with crucible temperature. By taking slopes of f, df/dt as a function of crucible temperature was evaluated as shown in the upper panel of Fig. S2(b), where the results for the other molecules are also presented. Further, by using Eq. (2) in the main

text, the rate of the adsorbed molecule number onto the quartz plate per unit area $dn_{\rm QCM}/dt$ were also evaluated, as shown in the lower panel of Fig. S2(b). It can be seen that, for each molecules, $dn_{\rm QCM}/dt$ increases exponentially with the crucible temperature. We confirmed that, for all molecules, the obtained $dn_{\rm QCM}/dt$ values can be fit by the equation based on the Arrhenius relation as,

$$\frac{dn_{QCM}}{dt} = N_0 v \, \exp\left(-\frac{\Delta H}{RT}\right) \tag{1}$$

where N_0 is the number of surface molecules, ν the attempt frequency, ΔH the enthalpy of sublimation, R the gas constant. The result guarantees that the crucible temperature in our home-build molecular evaporator can be precisely controlled, and the resulting evaporation rate can be accurately monitored by the QCM.



Figure S2: (a) f variation as a function of time during sublimation of H₂TPFPP molecules. (b) Dependence of the logarithm of df/dt (lower panel) and dn_{QCM}/dt (lower panel) on the inverse of the crucible temperature. The solid lines in lower panel show fits of the data by Arrhenius equation.