Local-Field-Induced Effective Magnetic Hysteresis of Molecular Magneto-Optical Effects in the Visible Region at Room Temperature: Phthalocyanine Thin Films on Ferromagnetic Inorganic Substrates

Kazuyuki Ishii and Kazutaka Ozawa*

Contribution from the Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba,

Meguro-ku, Tokyo 153-8505, Japan.

Supporting Information:

Bis(tri-*n*-hexylsiloxy){2,9(or10),16(or17),23(or24)-tetra-*tert*-butylphthalocyanato}silicon, $SiPc(OTHS)_2$[12]

Anal. Calcd for $C_{84}N_8H_{126}O_2Si_3$: C, 73.95; H, 9.31; N, 8.21. Found: C, 73.79; H, 8.76; N, 7.39. MALDI-TOF-mass m/z = 1362.3 (M^+), UV-vis (Toluene) λ/ nm ($\varepsilon/10^4$) 676 (33), 646 (3.9), 609(4.5), 356(9.4).

Cast films

For preparing thin films, 10 μL of ethanol solution containing 0.19 mM of $SiPc(OTHS)_2$ were dripped down onto an area determined by masking tapes ((10 × 15) and (5 × 15) mm^2 for Ni and $SrO{\cdot}6Fe_2O_3$ substrates, respectively). Although cast films prepared by using $CHCl_3$ or toluene were obviously inhomogeneous, the relatively homogeneous cast films were easily prepared by using EtOH as a solvent, which covered the most parts of the substrates. The thicknesses of the cast films (~20 and ~32 nm for Ni and $SrO{\cdot}6Fe_2O_3$ substrates, respectively) were evaluated from the molecular space of $SiPc(OTHS)_2$ (1.6 × 1.6 × 1.45 nm^3/mole evaluated from the optimized structure calculated using the PM3 Hamiltonian, Fig. 1) and the number of moles of $SiPc(OTHS)_2$, which was evaluated by extracting SiPc with toluene and measuring the absorbance at the Q band. This evaluation method was supported by a fact that the molecular space calculated was consistent with the nitrogen adsorption-desorption measurements.[13] The AFM measurements indicate that it was unfortunately difficult to determine the small thickness (a few tens of nanometres), since the roughness of the substrates was a few hundreds of nanometres.

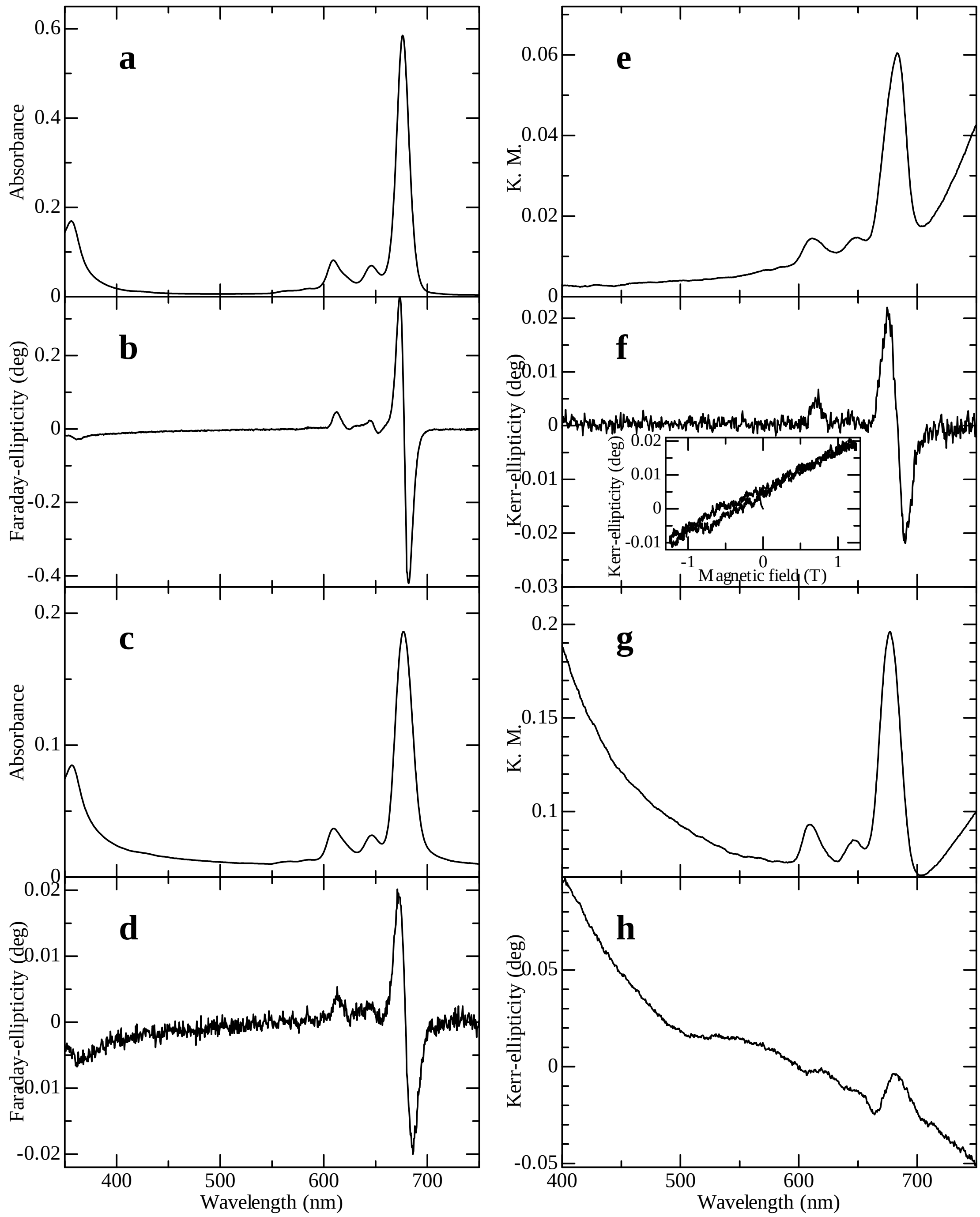

Fig. S1 Diffuse transmission (a, c), diffuse reflection (e, g), Faraday-ellipticity (b, d), and Kerr-ellipticity (f, h) spectra of $SiPc(OTHS)_2$. These spectra were measured in toluene solution (a, b), as a film on a glass substrate (c, d), as a film on an Al substrate (e, f), and as a film on a Ni substrate (g, h), respectively. The spectroscopic properties of thin films, such as the sharp Q absorption band and intense magneto-optical signal, are similar to those of toluene solution. Inset (f) shows the magnetic field dependence of Kerr-ellipticity (675 nm) in the case of $SiPc(OTHS)_2$ on the Al substrate. Because of the diamagnetic Al substrate, the magneto-optical signal increases in proportion to the external magnetic field strength.

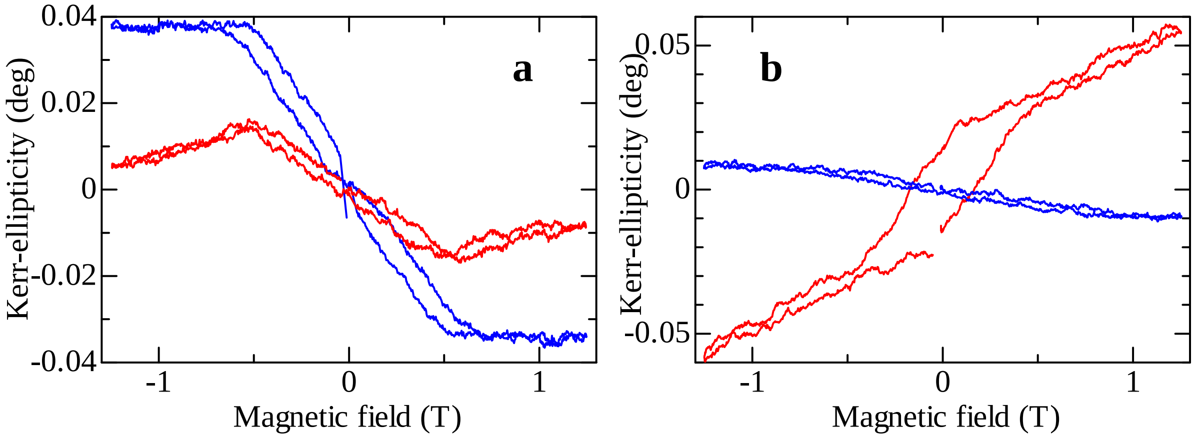

Fig. S2 Magnetic field dependences of Kerr-ellipticity (680 nm) for $SiPc(OTHS)_2$ films (red line) on Ni (a) and $SrO{\cdot}6Fe_2O_3$ (b) substrates. The blue lines show magnetic field dependences of Kerr-ellipticity (680 nm) for the Ni (a) and $SrO{\cdot}6Fe_2O_3$ (b) substrates. In the case of $SiPc(OTHS)_2$ on $SrO{\cdot}6Fe_2O_3$, the magnetic hysteresis (680 nm) of Kerr-ellipticity is clearly attributed to $SiPc(OTHS)_2$ interacting with $SrO{\cdot}6Fe_2O_3$ (Fig. 3f), since the magneto-optical signal due to $SrO{\cdot}6Fe_2O_3$ is negligibly small compared with that due to $SiPc(OTHS)_2$. In the case of Ni, the deduction is also meaningful, since the slope change by adding $SiPc(OTHS)_2$ is obviously larger at the low magnetic field region than that at the high magnetic field region.