Electronic Supplementary Information

Tuning the magneto-optical response of TbPc$_2$ single molecule magnets by the choice of the substrate

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Fig. S1. Maldi-ToF spectrum of [TbPc$_2$]$^0$ complex shows the parent ions at $m/z = 1183$. An expanded view of the peak shows an isotope distribution, which is in very good agreement with theoretical predictions.
Fig. S2. The UV/vis/nIR absorption spectrum is similar to the neutral green form of [LnPc2]0 spectra [D. Markovitsi, T.-H. Tran-Thi, Chem. Phys. Letters, 1987, 137, 107-112] with the most intense band - the Q-band - at 672 nm. In the near-infrared region two main bands are observed at about 906 nm and 1300-1800 nm. The shorter wavelength band is related to the radical part and attributed to the 1e_g(\pi)\rightarrow a_u(\pi) transition; the lower-energy band is assigned to an intramolecular charge transfer (CTI). Those signals are the fingerprints of the neutral species [LnPc2]0 and, thus, confirm their nature. All the near-infrared bands disappear upon reduction by hydrazine hydrate (1% vv).
Fig. S3. MOKE spectrum of a blank piece of Si(111) covered with native oxide.
Fig. S4. VASE (Variable Angle Spectroscopic Ellipsometry) spectra of the 62 nm TbPc$_2$ on SiO$_2$/Si sample. The green dashed lines belong to the experimental data and the red solid lines represent the model fit. The model consists of eleven Gaussian oscillators and a uniaxial anisotropy of the optical properties is assumed.
Fig. S5. Diagonal elements of the dielectric tensor in the plane (left) and the calculated off-diagonal elements (right) of TbPc$_2$ thin films on SiO$_2$/Si with different thicknesses. The values of the components of the dielectric tensor are normalized to a magnetic field of 1 T.
Fig. S6. Out-of-plane components of the dielectric tensor of five TbPc$_2$ films on SiO$_2$/Si.
Fig. S7. Complex refractive index of TbPc$_2$ films on PTCDA/SiO$_2$/Si.
Fig. S8. Complex refractive index of TbPc$_2$ films on Co/SiO$_2$/Si.
Table S1. Summary of the obtained Landé factors and ligand field (LF) parameters from fitting of the hysteresis loops at 1.8 K using the Hamiltonians below. For comparison the parameters for simulation from Ishikawa et al. [Ishikawa, N.; Sugita, M.; Okubo, T.; Tanaka, N.; Iino, T.; Kaizu, Y. Inorg. Chem., 2003, 42, 2440-2446] are shown. The Stevens coefficients used for the Tb$^{3+}$ ion are $\alpha = -1/99$, $\beta = 2/16335$ and $\gamma = -1/891891$. [Stevens, K.W.H. Proc. Phys. Soc. A, 1952, 65, 209] For having reasonable LF parameters it was necessary to include the Landé factor as a free parameter in the fitting procedure. Remarkable are the much higher LF parameters in the TbPc$_2$ film on silicon compared to the powder measurement and the simulation. This might be related to lower inter-molecular interaction in the film, compared to the powder.

\[
\vec{H}_{TbPc_2} = \vec{H}_{Zeeman} + \vec{H}_{lf}
\]

\[
\vec{H}_{Zeeman} = g_J \mu_B \mathbf{J} \cdot \mathbf{H}
\]

\[
\vec{H}_{lf} = A_2^0 < r^2 > + A_4^0 < r^4 > + A_6^0 < r^6 > + \gamma O_6^0
\]

<table>
<thead>
<tr>
<th></th>
<th>Simulation</th>
<th>43 nm TbPc$_2$/Si (Fit)</th>
<th>TbPc$_2$ Powder (Fit)</th>
<th>37 nm TbPc$_2$/PTCDA (Fit)</th>
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<tbody>
<tr>
<td>$g_J$</td>
<td>1.50</td>
<td>1.58</td>
<td>1.40</td>
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<tr>
<td>$A_2^0$ / cm$^{-1}$</td>
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<td>849</td>
<td>153</td>
<td>849</td>
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<tr>
<td>$A_4^0$ / cm$^{-1}$</td>
<td>-230</td>
<td>175</td>
<td>59</td>
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<tr>
<td>$A_6^0$ / cm$^{-1}$</td>
<td>35</td>
<td>49</td>
<td>101</td>
<td>49</td>
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</table>