Supplementary Information

Enhanced Magnetic Spin-Spin Interactions Observed between Porphyrazine-Derivatives on Au(111)

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Supplementary Note 1. Atomic coordinates of the optimized structure of phase I film of VOTTDPz molecules, which are the results of structural optimization with VASP. The coordinates of gold substrate is included. The coordinates are expressed with a POSCAR/CONTCAR format used in VASP calculation.

### SELECTIVE DYNAMICS

**Direct**

| Coordinates | T | T | T |
|-------------|---|---|---|
| 0.7088983716892593 0.5793057555143675 1.0036989304478201 | T | T | T |
| 0.9139246686421746 0.5793057555143675 1.0220874013514877 | T | T | T |
| 0.7303571838767248 0.434997380814798 1.0239580985358836 | T | T | T |
| 0.6006811783651576 1.2074092309988871 0.0441329328881612 | T | T | T |
| 0.763538371284240 0.4807942791966379 1.0105218378904928 | T | T | T |
| 0.7381046532122908 0.1101601508272972 0.030943735718181 | T | T | T |
| 0.685794159467117 0.672617238600176 0.0184543543015179 | T | T | T |
| 0.106429314656020 0.1357126721593221 0.064653910255855 | T | T | T |
| 0.046675040977448 0.6004296216062279 0.0347768647142444 | T | T | T |
| 0.2887060801157367 0.9716228089387676 0.016917739293498 | T | T | T |
| 0.1528901125464278 0.6144468720193124 0.0401150310807107 | T | T | T |
| 0.4194248240682253 0.9207998581087777 0.0307023323571971 | T | T | T |
| 0.2752217427850784 0.5637893043520129 0.0223276458497584 | T | T | T |
| 0.3950770197307346 0.8741403505284892 0.0472717965765799 | T | T | T |
| 0.2446010233237019 0.5159380526570966 0.0146006785276452 | T | T | T |
| 0.2567639381682038 0.8927849077659207 0.034735858470319 | T | T | T |
| 0.8542516842723202 0.3818130665265450 0.013624102873255 | T | T | T |
| 0.5709065385809321 0.0819677140219002 0.0228697532367216 | T | T | T |
| 0.9623102150357573 0.3936068828996521 0.0241611728613994 | T | T | T |
| 0.7067835516309181 0.0325094197582788 0.0106188730270807 | T | T | T |
| 0.1854643902768690 0.3663042830008564 0.01317363640534525 | T | T | T |
| 0.8550707137944547 0.930228032441171 0.0057716468868874 | T | T | T |
| 0.3246003122343220 0.3227038758824600 0.0434186762886827 | T | T | T |
| 0.8896478147498100 0.8767517056622238 0.005613263681811 | T | T | T |
| 0.3971466773207415 0.3549603515722479 0.000056561318171 | T | T | T |
| 0.0310406970802100 0.3383393338764170 0.0150022102602077 | T | T | T |
| 0.8241893343026277 0.6281730552420953 0.0222024972906140 | T | T | T |
| 0.1419955551648429 0.0373866622626831 0.0103664552874545 | T | T | T |
| 0.6116152008584647 0.6424850017029077 0.0969509069456369 | T | T | T |
| -0.036377550032476 0.1705819453664673 0.0126736974854323 | T | T | T |
| 0.301266440136301 0.4169914626300969 0.0000725367647624 | T | T | T |
| 0.08129010291595 0.873897621719047 0.01023296217553129 | T | T | T |
| 0.674828282918134 0.537193387548277 0.0126736974854323 | T | T | T |
| 0.78769258820233 0.364927345713078 0.01323054844555218 | T | T | T |
| 0.906903195622775 0.3520966597654009 0.0122029210251077 | T | T | T |
| 0.731675078675302 0.7646704457830528 0.00006516701903 | T | T | T |
| 0.173956112332604 0.423759621993312 0.014894430323510 | T | T | T |
| 0.974268994984664 0.919738715842323 0.0115660502162705 | T | T | T |
| 0.3341573608467117 0.4964703711377912 0.0000617302270191 | T | T | T |
Supplementary Note 2. Atomic coordinates of the optimized structure of phase II film of VOTTDPz molecules after the structural optimization with VASP. The coordinates of gold substrate is included. The coordinates are expressed with a POSCAR/CONTCAR format used in VASP calculation.

Selected dynamics

| Selective dynamics | Direct |   |   |
|--------------------|--------|---|---|
|                    | 0.9312121232347846 | 0.107938916372712 | 0.3270025270360293 | T | T | T |
|                    | 0.967524593200535 | 0.2417901954451916 | 0.3181423502286052 | T | T | T |
|                    | 0.9121391584332201 | 0.2141083911705266 | 0.3093454211882437 | T | T | T |
|                    | 0.074068818201269 | 0.889964237935602 | 0.3295183305256231 | T | T | T |
|                    | 0.9243604382495567 | 0.793572566258488 | 0.3593474658898413 | T | T | T |
|                    | 0.9368599977592494 | 0.9075580091781816 | 0.3437695678267919 | T | T | T |
|                    | 0.9347410262766687 | 0.297110555930151 | 0.302763262684723 | T | T | T |
|                    | 0.0243475706643110 | 0.238848744274412 | 0.344352729132869 | T | T | T |
|                    | 0.9514276919808751 | 0.7062502345154513 | 0.3477219622557747 | T | T | T |
|                    | 0.053427032599184 | 0.2931186416404295 | 0.3474738329488596 | T | T | T |
|                    | 0.08063575000367909 | 0.200969374383402 | 0.358574051696628 | T | T | T |
|                    | 0.0682526201003110 | 0.910528841505604 | 0.3438069053495529 | T | T | T |
|                    | 0.906282919834413 | 0.760128242336437 | 0.335105377208568 | T | T | T |
|                    | 0.4541923899786656 | 0.194508955662191 | 0.3142357184325767 | T | T | T |
|                    | 0.420418094300964 | 0.8331836202392724 | 0.286006908245538 | T | T | T |
|                    | 0.4599800205313682 | 0.827827178649983 | 0.2941210676223776 | T | T | T |
|                    | 0.501449805050609 | 0.725640215028590 | 0.2942706963729991 | T | T | T |
|                    | 0.5341292833236429 | 0.619933229351022 | 0.2890011602627851 | T | T | T |
|                    | 0.5667709296036934 | 0.650311941157605 | 0.2942221799033362 | T | T | T |
|                    | 0.5061308378097138 | 0.244446931957785 | 0.327056564575442 | T | T | T |
|                    | 0.4497914390588158 | 0.318796240050772 | 0.324877162126278 | T | T | T |
|                    | 0.5627642962176080 | 0.7767572374517826 | 0.3001128162173217 | T | T | T |
|                    | 0.406247778514758 | 0.9356294521083303 | 0.287345283959686 | T | T | T |
|                    | 0.4332305425725276 | 0.199297122098162 | 0.2982791445980624 | T | T | T |
|                    | 0.4819515896790776 | 0.3488136347890368 | 0.3347696829556585 | T | T | T |
|                    | 0.5068540150393869 | 0.1465544864911834 | 0.3152525171899111 | T | T | T |
|                    | 0.0374912830404597 | 0.5773647041672444 | 0.320187138653511 | T | T | T |
|                    | 0.595679427735697 | 0.146346054514347 | 0.3028331186500414 | T | T | T |
|                    | 0.6093960042292842 | 0.278787845433839 | 0.294388771977612 | T | T | T |
|                    | 0.5832043753199679 | 0.9593643656694535 | 0.3027483344878459 | T | T | T |
|                    | 0.070311439877118 | 0.7005729141147517 | 0.3061518988642504 | T | T | T |
|                    | 0.3352277549751610 | 0.9432160146264770 | 0.374296295669176 | T | T | T |
|                    | 0.3592015321951114 | 0.31520543475961 | 0.4138859296036919 | T | T | T |
|                    | 0.3267926033296657 | 0.313354511890375 | 0.3925182394055527 | T | T | T |
| X1         | Y1         | X2         | Y2         | X3         | Y3         |
|------------|------------|------------|------------|------------|------------|
| 0.687507762930360 | 0.7812461185034820 | 0.7013333333333324 | F | F | F |
| 0.7500084686513304 | 0.124995766743348 | 0.1701333333333324 | F | F | F |
| 0.7500084686513304 | 0.374995766743348 | 0.1701333333333324 | F | F | F |
| 0.7500084686513304 | 0.624995766743348 | 0.1701333333333324 | F | F | F |
| 0.7500084686513304 | 0.874995766743348 | 0.1701333333333324 | F | F | F |
| 0.8125091745602191 | 0.218745127198905 | 0.1701333333333324 | F | F | F |
| 0.8125091745602191 | 0.468745127198905 | 0.1701333333333324 | F | F | F |
| 0.8125091745602191 | 0.718745127198905 | 0.1701333333333324 | F | F | F |
| 0.850098802185136 | 0.062495598907432 | 0.1701333333333324 | F | F | F |
| 0.850098802185136 | 0.312495598907432 | 0.1701333333333324 | F | F | F |
| 0.850098802185136 | 0.562495598907432 | 0.1701333333333324 | F | F | F |
| 0.850098802185136 | 0.812495598907432 | 0.1701333333333324 | F | F | F |
| 0.8750095858768080 | 0.1562447070615960 | 0.1701333333333324 | F | F | F |
| 0.8750095858768080 | 0.4062447070615960 | 0.1701333333333324 | F | F | F |
| 0.9375105858768080 | 0.062495598907432 | 0.1701333333333324 | F | F | F |
| 0.9375105858768080 | 0.312495598907432 | 0.1701333333333324 | F | F | F |
| 0.9375105858768080 | 0.562495598907432 | 0.1701333333333324 | F | F | F |
| 0.9375105858768080 | 0.812495598907432 | 0.1701333333333324 | F | F | F |

The table continues in a similar format.
**Supplementary Note 3**

**Bulk structure deduced from XRD measurements in comparison with the film structure.**

We examine the structure of the bulk crystal in order to compare with that of the film. In Figure 1, we show a space filling view of the \( \beta \) phase VOTTDpz bulk crystal. The model is constructed from the crystallographic information file (CIF file) shown in the supplemental information of Ref. 1.

In this phase, VOTTDpz molecules are ordered with 2D pai interaction with neighboring molecules. Thus the centers of the molecules are distributed in a plane. As obvious from the top view, VO-up and VO-down molecules appear in an alternative manner. In addition it should be noticed that VO-up and VO-down molecules are tilted from the plane and show a buckled structure.

**Supplementary Figure 1.** A space filling view of the \( \beta \) phase VOTTDpz bulk crystal; top view (upper) and side view (lower). Light gray, dark gray, blue, yellow and red circles represent V, C, N, S and O atoms, respectively. Note that VO up and VO down molecules appear in an alternative manner.
Supplementary Note 4
XMCD measurement on VOPc and VOTTDPz

We compare the circular polarized x-ray absorption spectroscopy (XAS) obtained on the films of VO phthalocyanine (VOPc) and VOTTDPz molecules on Au(111). In each panel, XAS results for two circular directions and the XMCD plots are illustrated. The photon energy range includes V 2p and O 1s components. The XMCD intensity of the VOTTDPz component is doubled for the clarification. The XMCD intensity comparison between the VOPc film and the VOTTDPz film, by considering the doubled scale for the VOTTDPz film, indicates the magnetization is weaker for the VOTTDPz film.

Supplementary Figure 2. Circular polarized XAS of films of VOPc (a), and TbPc2 (b) on Au(111) at T=5 K and B=5 T at 0° (normal) and 55° incidence (I+, I-) and XMCD for each case. Note XMCD plot for VOTTDPz is doubled in y-scale.

Supplementary References
1. Miyoshi, Y; Takahashi, K; Fujimoto, T; Yoshikawa, H; Matsushita, MM; Ouchi, Y; Kepenekian, M; Robert, V; Donzello, MP; Ercolani, C, et al. Crystal Structure, Spin Polarization, Solid-State Electrochemistry, and High N-Type Carrier Mobility of a Paramagnetic Semiconductor: Vanadyl Tetrakis(Thiadiazole)Porphyrazine. Inorg. Chem. 2012, 51, 456-462.